CATALYZED-AIR OXIDATION OF THIOSALT EFFLUENTS USING COPPER SULFIDE CATALYSTS

FINAL REPORT

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SUMMARY

The residual thioanion constituents in copper sulfide mill tailings waters (thiosulfate ($S_2O_3^=$), tetrathionate ($S_4O_6^=$), and trithionate ($S_3O_6^=$)) are very slowly converted to sulfuric acid in the environment, causing an acid pollution problem. The possibility of using polymer-supported copper (II) catalysts for air oxidation of these thiosalts has been investigated in this laboratory in the past. Recently, it was discovered that copper sulfide ore concentrates could also catalyze the air oxidation of thiosalts to sulfate. This report examines the selection of the most active ore concentrate catalysts from materials supplied by CANMET. Kinetics of thioanion oxidation with such catalysts were investigated on a batch scale (Phase I), and subsequently used to help in the determination of optimum parameters for a laboratory scale continuous process (Phase II).

Preliminary catalyst activity measurements were made using an oxygen consumption apparatus whereby the largest initial rate of oxygen consumption in the oxidation of a thiosalt solution was used to identify the most promising catalysts for further study. Batch studies of these catalysts provided time-concentration profiles of reactants and products such that a reaction mechanism and kinetic parameters could be determined. Slurry-type stirred reactors were used in the final Phase for the selected catalysts to determine reagent consumption, catalyst life, etc.

Phase I

From the oxygen uptake experiments, it was found that Converter White Metal and Reverbatory Matte concentrates supplied

by Noranda were the most active catalysts of the materials supplied. For these catalysts, the initial rate of O_2 uptake was found to be first order with respect to oxygen and thiosulfate concentrations with overall activation energies of about 30 kJ/mol O_2. The acid generated by thiosalt oxidation was found to cause catalyst decomposition:

$$Cu_2S + 2\ H^+ + 0.5\ O_2 \longrightarrow CuS + Cu^{2+} + H_2O \qquad (1)$$

This reaction is first order with respect to H^+ concentration. The solubilized copper generated by this reaction can precipitate from solution in the form of basic copper sulfates such as brochantite ($3Cu(OH)_2.CuSO_4$).

For the batch studies of Phase I and the continuous work carried out in Phase II of the project, efforts were focussed on the Converter White Metal catalyst, which was chosen as the best overall catalyst for further development.

With the slurry batch reactor, the product distribution profiles indicated the following reaction scheme for thiosalt oxidation with Converter White Metal catalyst:

$$S_2O_3^{=} + 2\ O_2 + H_2O \longrightarrow 2\ SO_4^{=} + 2\ H^+ \qquad (2)$$

$$2\ S_2O_3^{=} + 0.5\ O_2 + H_2O \longrightarrow S_4O_6^{=} + 2\ OH^- \qquad (3)$$

Both of the above reactions are quite fast, and the initial products are a mixture of sulfate and tetrathionate. However, if the reaction pH is basic, tetrathionate rapidly converts to trithionate:

$$4\ S_4O_6^{=} + 6\ OH^- \longrightarrow 2\ S_3O_6^{=} + 5\ S_2O_3^{=} + 3\ H_2O \qquad (4)$$

As the pH drops to neutrality, trithionate is converted to sulfate and thiosulfate:

$$S_3O_6^{=} + H_2O \longrightarrow SO_4^{=} + S_2O_3^{=} + 2H^+ \qquad (5)$$

The thiosulfate generated in reactions (4) and (5) is reoxidized to tetrathionate and sulfate by reactions (2) and (3). Finally, there is a very slow oxidation of tetrathionate to sulfate:

$$S_4O_6^{=} + 3.5\ O_2 + 3\ H_2O \longrightarrow 4\ SO_4^{=} + 6\ H^{+} \qquad (6)$$

With an initial acidic pH, only reactions (2), (3) and (6) are important. Pseudo-first order rate constants are in the order of 10^{-2} to 10^{-3} min^{-1} at 30°C, and activation energies range from 34 kJ/mol to 50 kJ/mol for these reactions.

The reaction pH is an important parameter. The overall thioanion oxidation rates are relatively low above a pH of 6, whereas, with pH's below 4 the oxidative degradation of the catalyst according to reaction (1) became significant.

Phase II

The continuous runs with Converter White Metal catalyst generally confirmed the earlier batch and gas uptake results, however, there were some differences.

It was found that the slow oxidation of tetrathionate according to reaction (6) was the controlling factor in reactor residence time. Trithionate was also more difficult to oxidize than batch experiments seemed to indicate. With a 30 (catalyst weight / volume slurry) % slurry loading at 30°C with a 8 mM $S_2O_3^{=}$, 1.5 mM $S_4O_6^{=}$, and 1 mM $S_3O_6^{=}$ feed solution, a residence time of about 12 hours was necessary to reduce the effluent thiosalt level to 100 ppm or less. The optimal reactor pH for thioanion oxidation is about 5.0. The rate of oxidative catalyst decomposition (reaction (1)) was such that caustic neutralization of acid produced from thiosalt oxidation was not necessary for long periods of time (1 month). Such acid degradation was found

to cause a slow change of Cu_2S to CuS with time, the latter being much less active for air oxidation of thioanions. A catalyst life of greater than three months is predicted on the basis of the studies carried out.

For the final studies, real thiosalt effluent was obtained from Brunswick Mining and Smelting. It was found that the results obtained were quite similar to those obtained with the previous synthetic solutions, except the high Fe^{2+} concentration in these solutions precipitated out, at the optimal pH range for thioanion oxidation, as $Fe(OH)_3$. Although such precipitates caused numerous operational problems, the catalyst activity was not adversely effected. Consequently, Converter White Metal appears to be an effective catalyst for the air oxidation of thioanions present in mill tailings water effluents.

RESUME

Les montants résiduels de thio-sels présents dans les effluents des usines de traitement (thio-sulfate ($S_2O_3^=$), tétrathionate ($S_4O_6^=$) et trithionate ($S_3O_6^=$)) sont lentement transformés, dans l'environnement, en acide sulfurique ce qui cause un problème de pollution très sérieux. La possibilité d'utiliser des catalyseurs contenant du cuivre (II) supporté par un polymère pour l'oxydation en présence d'air de ces thio-sels a été étudiée auparavant par notre laboratoire. Récemment, il fut découvert que les concentrés de minerai de sulfure de cuivre peuvent eux aussi catalyser l'oxydation de thio-sels en sulfate en présence d'air. Ce rapport examine la sélection des catalyseurs de concentrés de minerai les plus actifs de ceux obtenus de CANMET. La cinétique de l'oxydation des thio-sels avec ces catalyseurs a été enquêtée à l'échelle "batch" (Phase I), et ces resultats ont été employés pour déterminer les paramètres optimums pour un procédé continu à l'échelle du laboratoire.

L'évaluation préliminaire de l'activité des catalyseurs a été faite à l'aide d'un appareil de consommation d'oxygène. Les catalyseurs avec les plus hauts taux initiaux de consommation d'oxygène furent choisi comme les catalyseurs les plus prometteurs. Les études "batch" de ces catalyseurs ont fourni des profils concentration-temps de réactifs et de produits qui nous ont permis de déterminer le mécanisme de réaction et les paramètres cinétiques. Des réacteurs de type agités furent utilisés avec quelques-uns des catalyseurs les plus prometteurs

durant la Phase finale de ce travail afin de déterminer la consommation de réactifs, la durée de vie du catalyseur, etc ...

Phase I

A l'aide de l'appareil de consommation d'oxygène, il fut découvert que le "Converter White Metal" et le "Reverbatory Matte", fournis par Noranda, étaient deux des catalyseurs les plus actifs de tous ceux reçus. Pour ces deux catalyseurs, le taux initial de consommation d'oxygène était de premier ordre en ce qui concerne la concentration d'oxygène et de thio-sulfate. Les énergies d'activation étaient environ 30 kJ/mol O_2 pour ces deux systèmes. L'acide produit lors de l'oxydation des thio-sels cause la décomposition du catalyseur:

$$Cu_2S + 2\ H^+ + 0.5\ O_2 \longrightarrow CuS + Cu^{2+} + H_2O \qquad (1)$$

Cette reaction est de premier ordre en ce qui concerne la concentration de H^+. Le cuivre soluble ainsi produit peut précipiter sous forme de sulfates de cuivre basiques tel le "brochantite" ($3\ Cu(OH)_2.CuSO_4$).

Pour les expériences "batch" commencées lors de la première Phase et les études entreprises dans la deuxieme Phase de ce travail, nos efforts furent dirigés vers le "Converter White Metal", qui fut choisi comme le catalyseur de choix.

Avec le réacteur "batch", les profils de distribution de produits indiquent que l'oxydation de thio-sels en présence du "Converter White Metal" se poursuit de la façon suivante:

$$S_2O_3^{=} + 2\ O_2 + H_2O \longrightarrow 2\ SO_4^{=} + 2\ H^+ \qquad (2)$$

$$2\ S_2O_3^{=} + 0.5\ O_2 + H_2O \longrightarrow S_4O_6^{=} + 2\ OH^- \qquad (3)$$

Ces deux réactions sont très rapides et les produits initiaux

sont une combinaison de sulfate et de tétrathionate. Cependant, si le pH est basique, le tétrathionate se transforme rapidement en trithionate et thio-sulfate:

$$4\ S_4O_6^{=} + 6\ OH^- \longrightarrow 2\ S_3O_6^{=} + 5\ S_2O_3^{=} + 3\ H_2O \qquad (4)$$

Lorsque le pH devient neutre, le trithionate est changé en sulfate et thio-sulfate:

$$S_3O_6^{=} + H_2O \longrightarrow SO_4^{=} + S_2O_3^{=} + 2\ H^+ \qquad (5)$$

Le thio-sulfate produit par les reactions (4) et (5) est oxydé en sulfate et en tétrathionate par les réactions (2) et (3), respectivement. Finalement, l'oxydation du tétrathionate directement en sulfate est très lente et s'accomplit de cette façon:

$$S_4O_6^{=} + 3.5\ O_2 + 3\ H_2O \longrightarrow 4\ SO_4 + 6\ H^+ \qquad (6)$$

Avec un pH initial acidique, seulement les réactions (2), (3) et (6) sont importantes. Les constantes de taux sont de pseudo-premier ordre et sont de l'ordre de grandeur de 10^{-2} à 10^{-3} min^{-1} à 30°C. Les énergies d'activation varient entre 34 kJ/mol et 50 kJ/mol pour ces réactions.

Le pH de réaction est un paramètre très important. Les taux d'oxydation des thio-sels sont relativement lents au-dessus d'un pH de 6; au-dessous d'un pH de 4, l'oxydation et la décomposition du catalyseur selon la réaction (1) deviennent considérable.

Phase II

En général, les expériences continues à l'échelle du laboratoire avec le "Converter White Metal" ont confirmé les résultats obtenus avec l'appareil de consommation d'oxygène et le

réacteur "batch". Cependant, il y avait quelques différences.

Il fut découvert que l'oxydation très lente du tétrathionate selon la reaction (6) était le facteur qui contrôle le temps de résidence requis dans le réacteur. Aussi, le trithionate était plus difficile à oxyder que les résultats obtenus à l'aide des expériences "batch" nous avaient laissé entendre. Avec un chargement de catalyseur de 30 (masse du catalyseur/volume de slurrie) % à 30°C et avec une solution contenant 8 mM $S_2O_3^=$, 1.5 mM $S_4O_6^=$ et 1 mM $S_3O_6^=$, une période de résidence d'environ 12 heures était nécessaire pour réduire le niveau de thio-sels dans l'effluent à 100 ppm ou moins. Le pH optimum pour l'oxydation des thio-sels est environ 5.0. Le taux de décomposition du catalyseur (réaction (1)) était tel que la neutralisation (à l'aide de caustique) de l'acide produit lors de l'oxydation des thio-sels n'était pas nécessaire pour de longues périodes de temps (1 mois). Cette dégradation acidique du catalyseur cause le changement très lent du Cu_2S au CuS. Ce dernier est beaucoup moins actif que le Cu_2S envers l'oxydation de thio-sels en présence d'air. Une vie active de plus de trois mois est envisagée pour le catalyseur vu les études entreprises.

Pour les enquêtes finales, de l'effluent de thio-sels réel fut reçu de Brunswick Mining and Smelting. Les résultats obtenus avec cet effluent étaient très semblables à ceux obtenus avec les solutions synthétiques utilisées auparavant, sauf que le niveau élevé de Fe^{2+} dans l'effluent réel a été précipité sous forme de $Fe(OH)_3$ au pH optimum de 5. Même si la formation de ces précipités ont causé plusieurs problèmes d'opération, l'activité du catalyseur ne fut pas affecté de facon négative par eux. Par

conséquent, le "Converter White Metal" semble être un catalyseur efficace pour l'oxydation, en présence d'air, des thio-sels trouvés dans des effluents provenant d'usines de traitements.

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1. INTRODUCTION

1.1 Background

Partially oxidized sulfur oxyanions such as thiosulfate ($S_2O_3^=$), tetrathionate ($S_4O_6^=$) and trithionate ($S_3O_6^=$), which are collectively known as thiosalts, are formed during milling and flotation processing of sulfide ores. These residual constituents in mill tailings waters, when discharged into river systems, are converted sufficiently rapidly into sulfuric acid by bacterial action, resulting in an environmental pollution problem (1, 2). Complete oxidation of the thiosalts to sulfuric acid by chemical or biochemical means and neutralization of the acid by lime prior to discharge of the effluent to receiving streams has long been considered a viable solution to the problem, subject to development of a simple and economic means of oxidation of thiosalts in large volumes of waste water. In this context the possibility of using catalyzed air oxidation of thiosalts to sulfate became the subject of active research and investigation ever since the finding of the ability of suitably complexed copper (II) ions to catalyze, homogeneously, the oxidation of thiosulfate to sulfate by molecular oxygen (3). Research efforts were directed at developing polymer-supported catalysts having this property as this would facilitate economic recovery and reuse of the catalyst, and thus provide a potentially low cost method for removal of thiosalts.

A number of polychelates were prepared and tested for their catalytic activity for thiosalt oxidation by molecular oxygen. This led to the development of poly(4-vinyl pyridine)-Cu(II)

complexes as effective catalysts for this reaction (4, 5). Subsequent attempts to improve the activity and stability of these PVP-Cu(II) catalysts succeeded in developing a PVP-Cu(II) complex of optimum composition based on a quantitative understanding of the relation between catalytic activity and distribution of different coordinate species in the polychelate (6). Further enhancement of activity and stability of the complex was then achieved by cross-linking quaternization of the residual free pyridine units in the complex of optimum composition (7).

Though the aforesaid polymer-supported copper (II) catalysts showed high activity and stability in batch oxidation runs lasting a few hours, continuous oxidation runs conducted over several weeks, using continuous stirred tank (slurry) reactors and air as both the source of oxygen and a means of agitating the slurry, showed (8) that these catalysts undergo slow deactivation with time due to leakage of copper ions and slow but irreversible degradation of the polymer base. A subsequent search for other polymeric ligands capable of forming more stable copper complexes led to the use of polythiosemicarbazide (9) which is known to form very stable copper complexes having oxidation-reduction properties (10). Studies on thiosalt oxidation using such polythiosemicarbazide-Cu(II) complexes provided an indication that sulfur-bonded copper might be catalytically active for thiosalt oxidation by molecular oxygen. This was later confirmed by employing copper mercaptide as well as CuS and Cu_2S as catalysts for thiosalt oxidation by oxygen. Although CuS is rare

in nature and is somewhat difficult to prepare, Cu_2S is locally abundant and is also a common product of copper smelting (white metal). The possibility of using abundant chalcopyrite ($CuFeS_2$) concentrates was also investigated. Keeping in view the possibility of practical application of such a process, a study was undertaken of the product distribution pattern and kinetics of oxidation of the two predominant thiospecies, namely, thiosulfate and tetrathionate, using CuS, Cu_2S, and chalcopyrite concentrates from several sources as catalysts and air as the oxidizer. Oxidation runs were also performed over several weeks with a stirred tank reactor employing a slurry of concentrated copper ore as catalyst to gain information on the stability of the catalyst system (11).

1.2 Scope and Objectives of Present Study

In previous work (11), CuS, Cu_2S, and certain copper sulfide ore concentrates were examined as catalysts for thiosalt oxidation on a batch and continuous basis. The results obtained from these studies indicated that relatively inexpensive and readily available ore concentrates had potential for the development of effective thiosalt oxidation catalysts.

In an extension of these initial findings, the present study was initiated to identify the most catalytic active materials, from several common ore concentrates supplied by CANMET, and to extensively examine these selected catalysts under both batch and continuous conditions. From such studies, it was anticipated that sufficient data could ultimately be obtained to identify the most important reaction parameters and critical operation

conditions for the design of a feasible full scale process using these catalysts.

The present study was divided into two phases as described below:

Phase I

a) Various natural and synthetic copper sulfide ores were to be evaluated for their relative catalytic activity on the basis of their rate of initial oxygen uptake in reaction with a given thiosulfate solution.

b) The most active copper sulfide materials identified in (a) were to be used to identify optimum reaction parameters including particle size, agitation, pH, thiosalt effluent flow, temperature, pH control reagent, O_2 partial pressure, and retention time. The above effects were to be evaluated using oxygen uptake, batch and continuous methods.

c) Suitable reactors were to be evaluated for oxidation under the preferred conditions.

Phase II

Long term continuous runs were to be made with the selected reactor design and catalysts to maximize performance and to provide an initial evaluation of the critical parameters on a mini pilot scale. In addition, data was to be collected for reagent consumption (caustic, catalyst), temperature, retention time, etc... that might be important for the preliminary costing of the process. Initial work was to be carried out with

synthetic solutions, but later tests were to be carried out with real effluent obtained from Brunswick Mining and Smelting.

This report provides the results obtained in answer to the above noted objectives.

2. EXPERIMENTAL

2.1 Equipment and Procedure

2.1.1 Gas Uptake Apparatus and Procedure

The initial catalyst screening experiments for thioanion oxidation in the presence of oxygen were made by measuring the rate of oxygen uptake at constant temperature and pressure using the gas uptake apparatus shown in Figure 1.

The reaction slurry was contained in the 20 mL round bottom flask A which was clipped to a metal piston rod driven by a variable speed electric motor. The flask was immersed in a thermostatted bath which consisted of a four liter beaker containing silicon oil (Dow Corning 550 Fluid). The beaker was well lagged with asbestos-medium fiber and synthetic sponge and enclosed by a plywood box constructed with a sight window for viewing the reaction flask. An insulating cover on the top of the oil bath was made of polystyrene foam. Efficient stirring together with a 40 watt elongated light bulb as a heater enabled control of the bath temperature to within $\pm$ 0.02°C.

The reaction flask A was connected by a length of glass tubing containing two spring coil arrangements and a tap D, to a capillary manometer E. The manometer contained n - dibutyl phthalate (a liquid of negligible vapour pressure) and was in turn connected to the gas burette F, which contained mercury and a precision bore tubing G of known diameter. Both the capillary manometer and the gas burette were immersed in a constant temperature (25.0°C) rectangular water bath constructed of

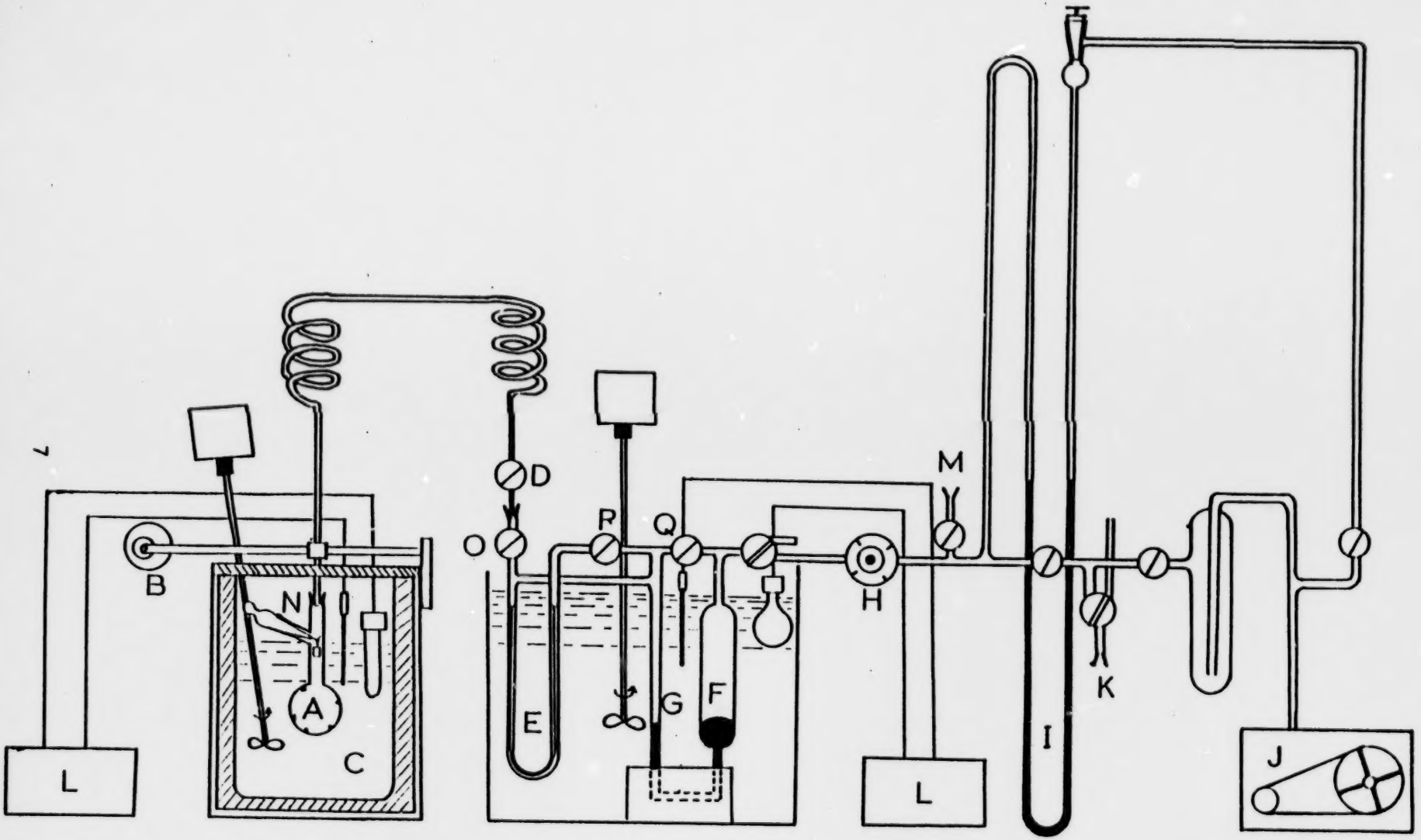


Figure 1. Constant Pressure Gas Uptake Apparatus.

Perspex. The gas burette was connected by means of an Edward's high vacuum needle valve H to a glass gas-handling system. This consisted of a mercury manometer I and connections leading to a Welch Duo Seal rotary vacuum pump and the glass inlet K.

The procedure used for a gas uptake experiment was as follows: A known amount of distilled water and catalyst (the catalyst was washed three times with distilled water, suction filtered, and allowed to dry overnight before use) were accurately measured into the reaction flask A. The desired amount of the reactant (i.e. sodium thiosulfate, $Na_2S_2O_3.5H_2O$) was accurately weighed into a Pyrex glass bucket; this was hooked onto an extended ground-glass cone and fitted into the side socket N of the reaction flask. Thus the reaction could be started when desired by turning the cone allowing the bucket to fall into the solution. The flask A was fitted with the spiral tubing containing tap D which was attached at position M. The solution was degassed twice by repeated freezing and warming under vacuum. Oxygen at a pressure somewhat greater than the water vapour pressure was then admitted through tap K to the reaction flask. The reaction flask, together with the spiral tubing, was then disconnected from M and attached to the capillary manometer at O with the reaction flask immersed in the thermostatted oil bath C and clipped to the piston rod. The remainder of the system beyond tap D was then evacuated and oxygen (Linde, technical grade) was introduced through tap K to a pressure slightly less than the desired pressure of the reaction. Tap D was then opened and the pressure adjusted to the desired reaction pressure by the introduction of gas through tap K. The

shaker was then started and the reaction flask left shaking for about 30 minutes to insure equilibrium between the oxygen dissolved in the solution and that of the gaseous phase. Taps P and Q were then closed and the glass bucket with its contents was allowed to fall into the solution. The shaker and a Lab-Chron timer were then started simultaneously. As the reaction proceeded and oxygen was consumed, the oil level in the left limb at the capillary manometer E began to rise. The manometer was balanced to the initial pressure by introducing gas into the burette through the needle valve H. The rise in the mercury level in the tube G was measured at suitable intervals by means of a vertically mounted Precision Tool cathetometer (model 2158). Since the diameter of the tube G was known, a direct measure of the volume of the gas consumed was obtained and a plot of gas uptake as moles of O_2 at S.T.P. against time could be drawn.

After completing the uptake experiment, the resulting solution (after decanting the settled catalyst) was promptly analyzed for the various thiospecies ($S_2O_3^=$, $S_3O_6^=$, $S_4O_6^=$), sulfate, copper and pH. If the solution could not be analyzed immediately, it was frozen until the analysis could be performed.

2.1.2 Batch Reactor

Batch reactions were carried out to elucidate thiosalt oxidation reaction mechanisms and kinetics.

Equipment

The batch apparatus is shown in Figure 2. The reactor consisted of a 3-necked flask partially submersed in a constant temperature water bath. A Teflon paddle, connected by a glass shaft to a Canframo stirrer (model RZR1-64), provided agitation for the reaction slurry. A thermometer was fitted in one side arm, or optionally a pH probe (Canlab H5503) connected to a Fisher Accumet pH meter/controller (model 650). Air was sparged through a 6.25 mm ID glass tube inserted in the other side arm and was presaturated with water (saturation assembly not shown) to lessen evaporation from the slurry.

Procedure

For a typical run, 400 mL of distilled water was placed in the reaction flask and allowed a few minutes to come to the set bath temperature. The stirrer was turned on (set to 700-800 rpm) and air sparging was also started (about 0.6 L/min). A weighed amount of catalyst was then added to the flask. The pH of the resulting slurry was noted if the catalyst was "used" and a sample taken for residual thiosalt and sulfate determination. A weighed amount of $Na_2S_2O_3.5H_2O$, calculated to give the desired initial thiosulfate concentration, was then added to the slurry and the start time noted. Samples of slurry were taken for

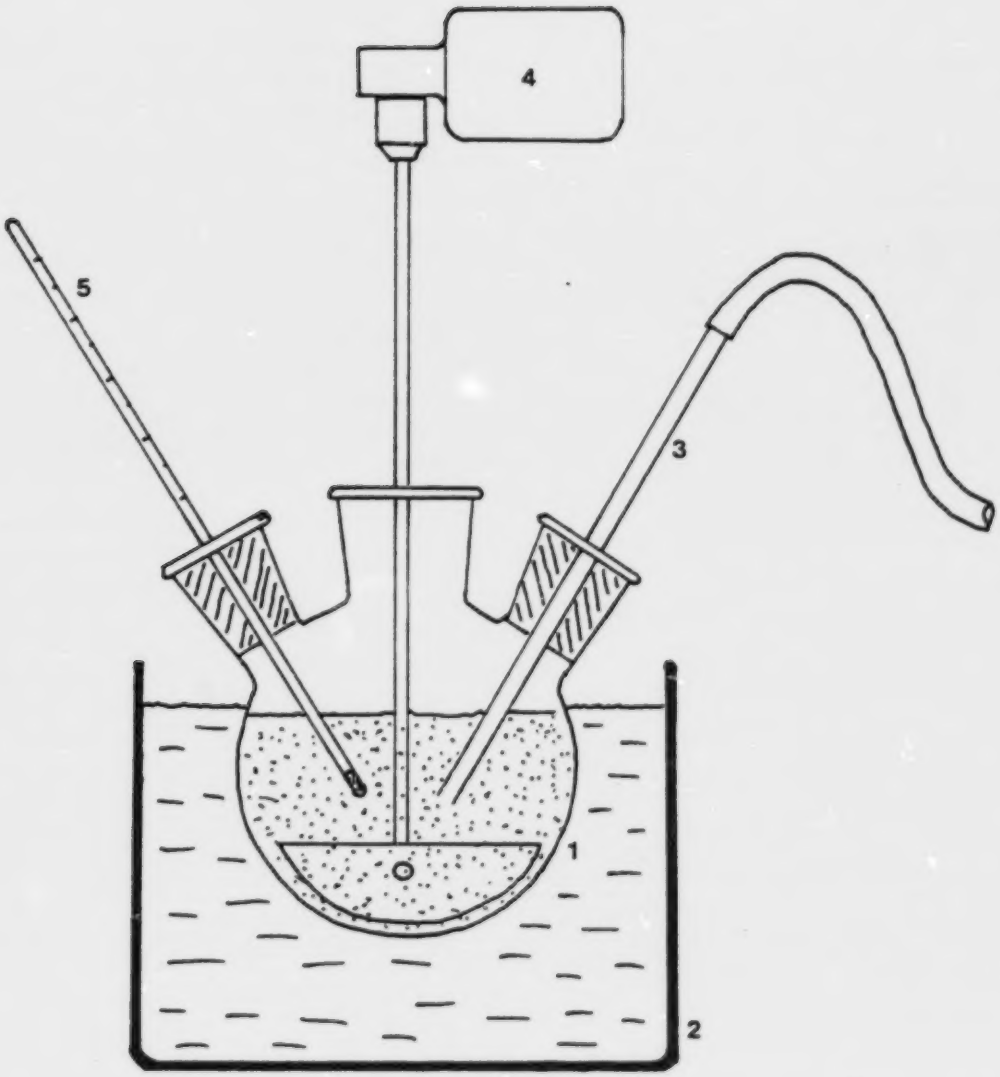


Figure 2. Batch apparatus. 1 - 500 mL reaction flask; 2 - constant temperature bath; 3 - air dispersion tube; 4 - stirrer motor; 5 - thermometer

analysis at 15, 30, 45, 60, 90, 120, 150, 195, and 240 minutes.

At each sample time, a 10 mL Mohr pipette was used to transfer a 2 mL slurry aliquot into each of three 50 mL volumetric flasks for determination of thiosulfate, trithionate, and tetrathionate. A separate 10 mL aliquot was placed in a fourth flask for analysis of sulfate. All slurry aliquots were filtered (Whatman #1) into the flasks and the residual catalyst rinsed with a few portions of distilled water. The slurry pH was also noted. Occasionally throughout the run, a separate sample of about 10 mL of filtered slurry was taken for soluble copper determination. At the end of the run, the samples gathered were analyzed and the results plotted to obtain a time - concentration profile.

In later batch work, synthetic solutions containing polythionates in varying proportions (and other added salts) and real thiosalt wastewater were examined. In these cases, 400 mL of the solution was placed in the flask and after the desired temperature was reached, catalyst was added to start the run.

2.1.3 Continuous Slurry Reactors

Equipment

Two types of reactors were possible for continuous studies: a catalyst bed type reactor and a slurry-type stirred tank reactor (STR). Because of the relatively long retention time (12 - 24 hours), the STR seemed much more practical for laboratory scale experiments. In addition, the intrinsic catalyst kinetics would be much easier to see with this type of reactor compared to

a bed reactor where such parameters as channelling, mass transfer, etc. would be of considerable concern. A STR continuous apparatus was also a natural extension of successful batch studies and most easily related to those results.

Although of similar design, three different reactors were used during this investigation. These were a stainless steel (SS) model of 10 L capacity; a corrosion-resistant PVC reactor; and a modified PVC reactor equipped with a catalyst settler for high slurry loading runs.

Stainless Steel Reactor

The basic layout for the continuous slurry reactor system is shown in Figure 3. The body of the reactor, constructed previously (8), was made of 304 SS (1.6 mm thickness). The shell (21 cm dia. x 43 cm) was fitted with five rows of staggered 1 cm diameter holes near the top under which there was a circular drip tray (see Figure 4). These holes were covered with a band of filter cloth, a layer of sheet filter paper (Whatman #1), and a secound layer of cloth, all held in place with a SS mesh band. With this arrangement, catalyst was kept within the reactor and effluent collected in the drip tray. Since severe corrosion was encountered in initial runs, the SS mesh band was replaced with one made of 1.6 mm Teflon sheeting perforated with 0.5 cm holes, and the filter hole area coated with a thin layer of Dow Corning Silicon Sealant.

The reactor interior was equipped with four full length baffles (1.5 cm wide x 1.6 mm thick). The stirrer consisted of a

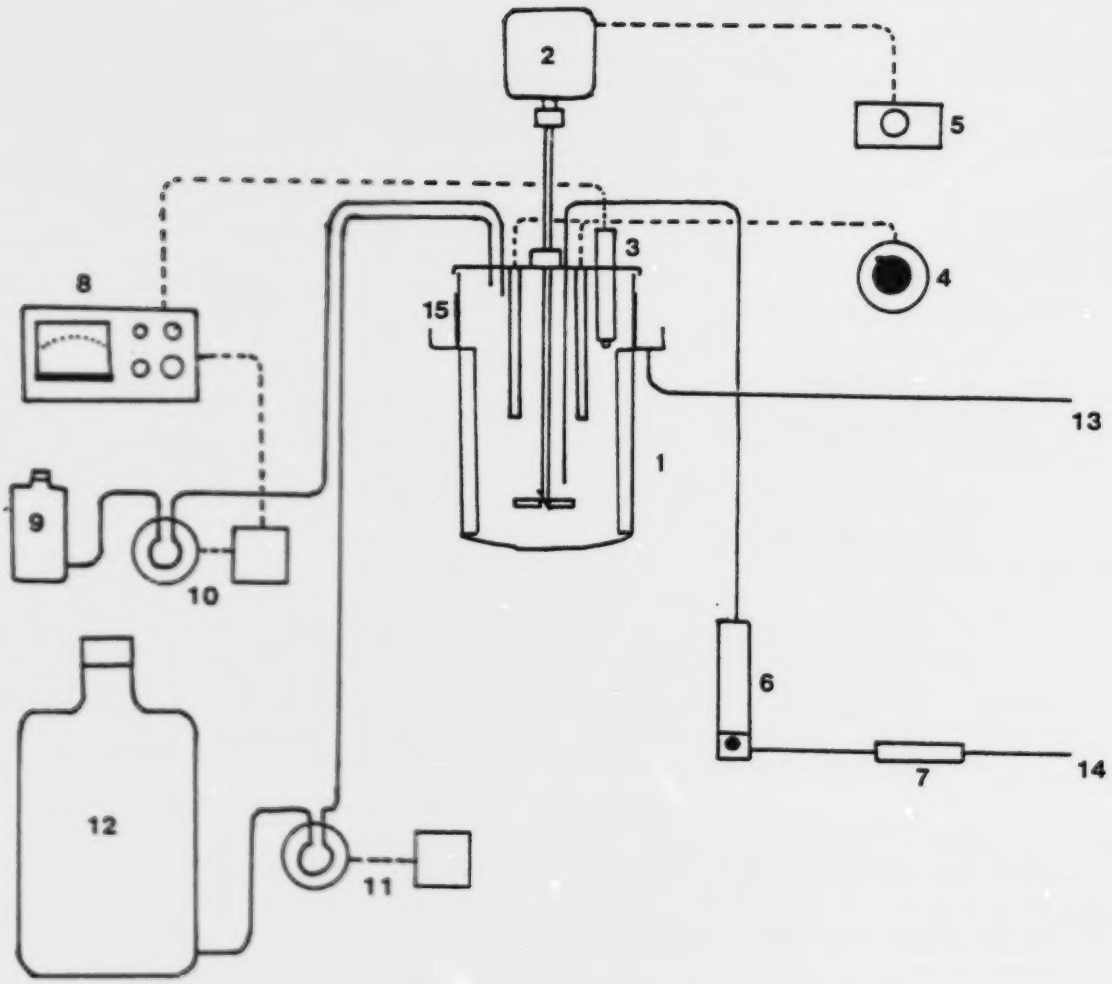


Figure 3. Stainless steel continuous reactor. 1 - reactor body; 2 - DC motor; 3 - pH probe; 4 - heater rheostat; 5 - motor speed control; 6 - rotameter; 7 - activated carbon trap; 8 - pH meter/controller; 9 - 10% NaOH supply tank; 10,11 - peristaltic pumps; 12 - 50 L feed tank; 13 - effluent (to drain); 14 - service air in; 15 - reactor effluent filter.

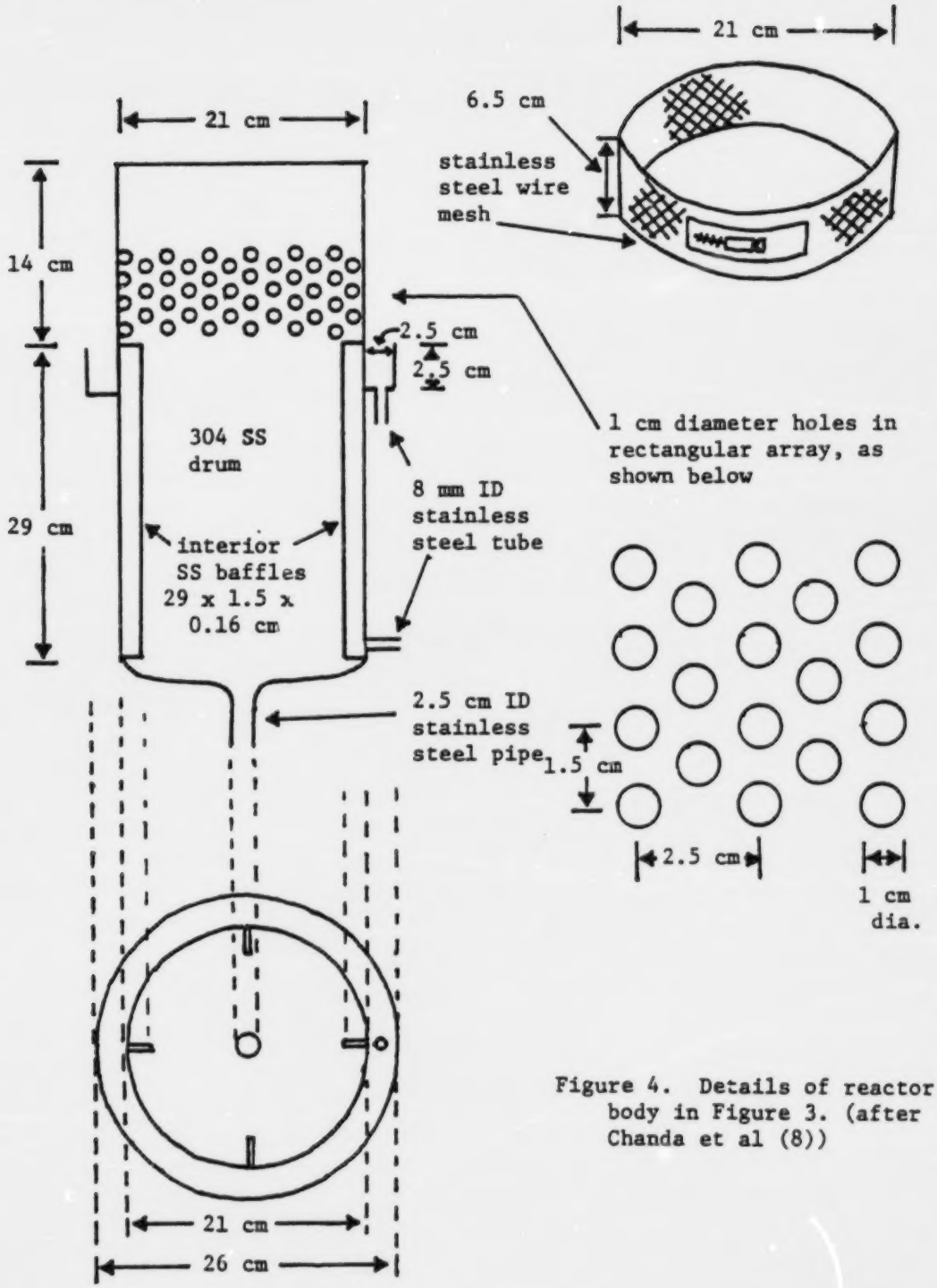


Figure 4. Details of reactor body in Figure 3. (after Chanda et al (8))

SS shaft (63 cm x 0.95 cm dia.) fitted with a 4 blade marine type propeller (10.2 cm dia., 30° blade pitch) connected to a Bodine Electric Co. model NSW-54 variable speed DC motor. Typically, the speed was set to the maximum without overloading the motor (about 800 rpm). The slurry flow was directed downwards from the propeller and then swept upwards along the reactor wall. This flow pattern serves to keep catalyst particles suspended (13); this was confirmed by slurry density measurements at the top and bottom of the reactor.

Air was introduced via a tube (6.4 mm id.) to the propeller intake. This aided oxygen transfer, although the propeller efficiency was lowered somewhat through a cavitation effect. The standard service air passed through an activated carbon trap and was metered by an Ametek LO-FLO rotameter (0 - 2 L/min).

Slurry temperature was controlled by two heating bars connected to a Variac power supply. The steady state temperature was determined by the Variac setting. A pH probe (Canlab H5503) dipped into the slurry and was connected to a Fisher Accumet pH controller (model 650) which maintained a set pH by addition of 10% NaOH through a Cole-Parmer peristaltic pump.

The feed solution was stored in a 50 L Nalgene tank, and metered into the reactor by a Watson-Marlow HR Flow Inducer peristaltic pump.

O_2 Mass Transfer

For heterogeneous reactions, mass transfer of reactants must always be considered. In a three phase (gas-liquid-solid) system, the transfer of gas can easily be a limiting step if the

gas is sparingly soluble, as in the present case. For the current study, the interest was in intrinsic catalyst activity , so mass transfer (MT) effects were to be minimal.

The reactor $K_L a_L$ (gas-liquid MT coefficient) was determined by the method of de Waal and Okeson (14) and $K_c a_s$ (liquid-solid MT coefficient) by correlations derived by Harriot (15). The method and calculations are shown in Appendix I. It was found that under the given reactor conditions and catalyst activity oxygen transfer was not a limiting factor in the overall reaction rate.

PVC Reactor

Due to corrosion problems with the stainless steel reactor in preliminary continuous runs, a PVC reactor was constructed. The reactor body had the same design and essential proportions as the SS model except 0.6 cm thick PVC was the material of construction. The propeller stirrer had a steeper pitch (40^{o}) and was powered by a 1140 rpm AC motor (GE model 5KH33GG 126ES); both of these changes improved dispersion for higher slurry loadings. With the higher motor speed, the dissipated stirring energy was sufficient to provide any desired temperature; a cooling coil with water flow controlled by an electromechanical valve connected to a Fisher Unitized Bath Control maintained the set temperature value.

The other support equipment was the same as for the SS reactor.

PVC Reactor - Settler

Later on in the slurry reactor research, much higher catalyst loadings were used (30 w/v %). With these slurries, it was not possible to use an effluent filter as it clogged up too quickly, so a catalyst settling system was devised (see Figures 5 to 7). A reactor overflow tube was connected to the settler which had an overall 20 minute residence time. The settled catalyst was returned to the reactor by a Cole-Parmer peristaltic pump. The recycle rate was high (1 L/min) as the catalyst particles quickly plugged the return tube if the linear velocity was too low.

The settler was fairly efficient; only about six grams of fine catalyst (0.2% of total) was lost per day. This lost material could be recovered by directing the settler outflow to a large (50 L) glass container for further settling. Usually more than 10 hours were needed for a completely clear supernatant.

A more powerful AC stirring motor (GE 5XBH002D, 250 watts) was used to keep the dense slurry in suspension. Measurements of the temperature and flow of cooling water indicated that 80 watts of stirring energy was dissipated in the 10 L reactor.

Procedure

Slurry reactor operation could be divided into four stages: (1) start-up period; (2) steady-state operation; (3) parameter changes; and (4) shutdown.

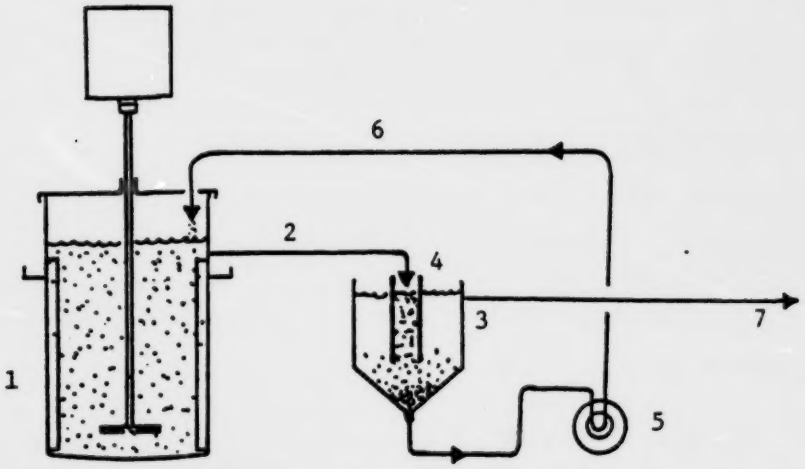


Figure 5. PVC reactor - settler schematic. 1 - reactor; 2 - reactor overflow tube; 3 - settler; 4 - feed well; 5 - peristaltic pump; 6 - catalyst return tube; 7 - effluent to drain or 50 L glass container.

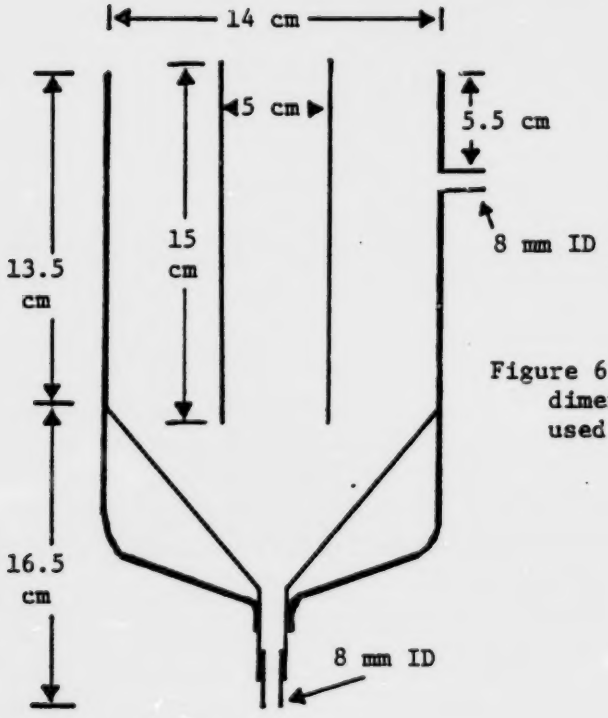


Figure 6. Settler detail and dimensions. Polyethylene is used throughout.

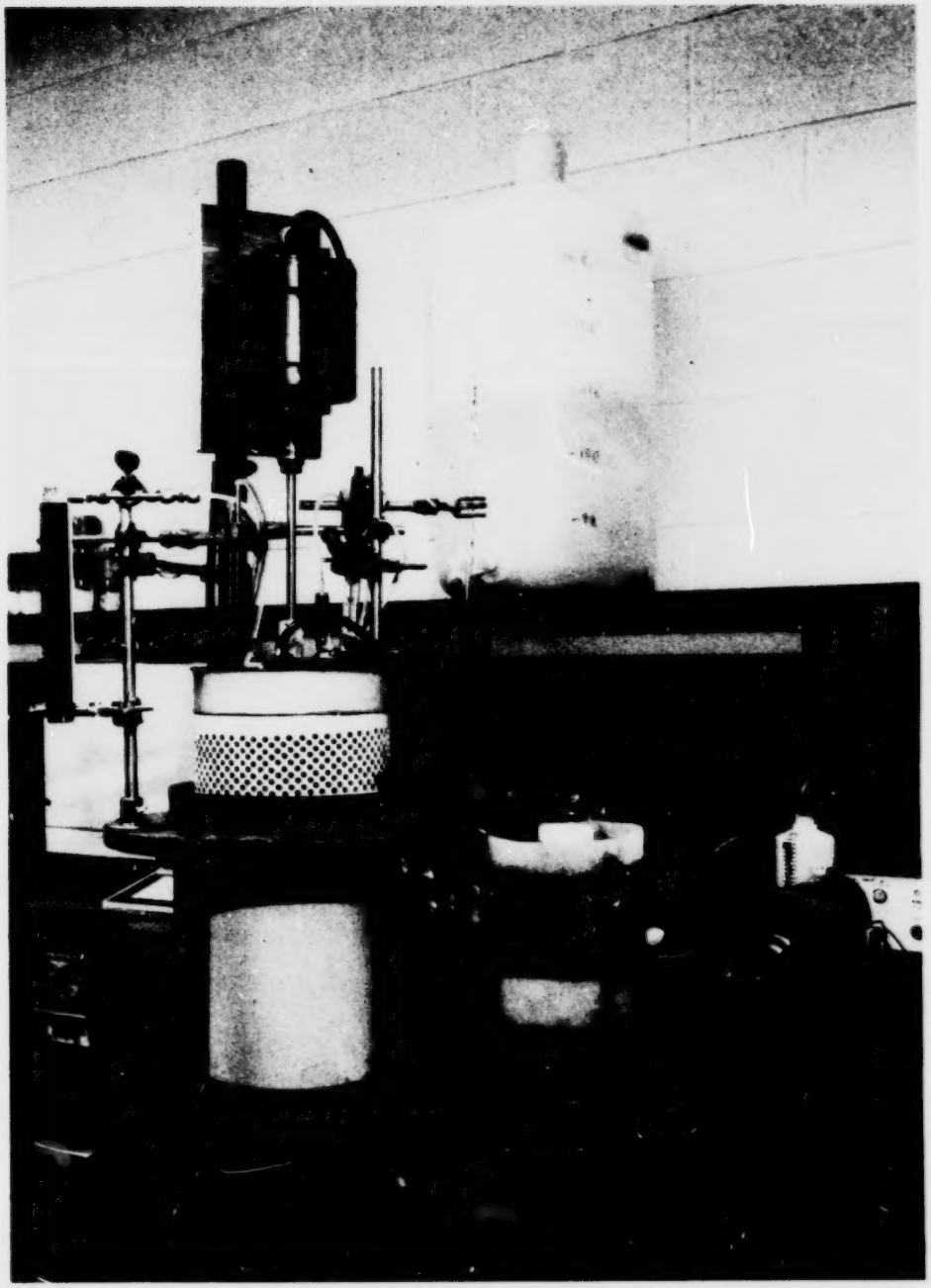


Figure 7. PVC reactor and settler apparatus

Start-up period

The start-up phase was the time necessary before steady state operation was achieved. Initially, the reactor was filled with the feed solution, the stirring started, and the catalyst slowly added. The reactor temperature, feedflow and air flow were then adjusted to the desired values. Equipment malfunctions were most frequent during this period so these parameters were rechecked frequently and changes made as necessary. Typically, the reactor settled down to steady state operation within a day.

Steady State Operation

The term "steady state" was applied when the reactor effluent composition was essentially constant over many days of operation, as opposed to hourly changes during start-up.

Effluent samples were taken daily in 150 mL plastic jars. The pH of the solution was recorded and aliquots taken for analysis of thioanions, sulfate, and soluble copper and iron. Usually, samples were collected over several days before analysis; during the interim the jars were kept at less than 4°C in a refrigerator. For longer storage, samples were frozen.

Reactor parameters such as temperature, air flow, feed flow and pH were also noted daily. All these data (analytical and reactor parameters) were recorded in a "Continuous.Reactor Data" sheet for each run.

Parameter Changes

Reactor variables (e.g. pH, flow rates) were occasionally

changed to determine their effect on the overall thiosalt oxidation. Usually, one variable was changed at a time and several days allowed for the reaction to come to a new steady state.

Shutdown

At the end of the run, all systems were shut off and the slurry drained into a 50 L glass vessel. After sitting for 1-2 days, the supernatant was drawn off and the settled catalyst collected. This "used" catalyst was suctioned filtered, rinsed, dried, weighed, and stored in four litre jars. These catalysts were saved for further analysis and/or reuse in subsequent runs.

2.2 Analytical Methods

2.2.1 Routine Analysis

Thiosulfate, trithionate, and tetrathionate were determined photometrically by the method of Mizoguchi and Okabe (16). Sulfate was analyzed by a Ba^{2+} precipitation / EDTA back titration method developed by Rolia and Barbeau (17). Soluble copper and iron were determined photometrically as the hexaamine and hexathiocyanate complexes, respectively. All measurements were carried out on either Perkin-Elmer Lambda 3B UV/VIS or Varian Cary model 219 spectrophotometer.

A Radiometer PHM61 pH meter fitted with a Canlab combination electrode (H5503) was used for all routine pH measurements.

2.2.2 Non-Routine Analyses

Some selected catalysts were examined by X-ray diffraction for composition and structure. This work was graciously done by CANMET. Total sulfur in catalysts was determined by a bromine oxidation technique (18).

2.3 Materials

2.3.1 Catalysts

Various copper sulfide materials were supplied by CANMET for initial evaluation (see Table 1). Those samples not sized as received (e.g. synthetic CuS) were ground to less than 150 μm before use.

For continuous runs, large amounts of the most promising catalysts were required. Thirty kilogram lots of Converter White Metal and Reverbatory Matte were obtained from Noranda. The large chunks were broken down by hand and then ground by an Alpine model C100LU grinder to a fine powder. This was sieved to obtain the desired fraction size.

2.3.2 Reagents

The chemicals used in this investigation are summarized in Table 2. Potassium trithionate was prepared by the method employed by Hitchen (19). All materials were used without further purification. Synthetic feed solutions were prepared using "softened" tap water, whereas distilled water was used for all analytical solutions.

Table 1. Copper Sulfide Materials
(supplied by CANMET)

Sample	Description
1	Natural CuS (covellite), $\leq$ 120 mesh
2	Synthetic CuS
3	White Metal (Hudson's Bay Mining & Smelting)
4	Copper Matte (Cu-Fe-S), $\leq$ 100 and $\geq$ 150 mesh
5	Synthetic Cu_2S, $\leq$ 325 mesh
6	Synthetic Cu_2S, $\leq$ 200 mesh
7	Synthetic Cu_2S, $\leq$ 150 mesh
8	Synthetic Cu_2S, $\geq$ 100 mesh
9	Chalcocite flotation concentrate, $\leq$ 325 mesh
10	Chalcocite flotation concentrate, $\geq$ 325 mesh
11	Copper concentrate (Cu_2S + Ni_3S_2), $\leq$ 120 mesh
12	Chalcopyrite ($CuFeS_2$), $\geq$ 100 mesh
13	Boronite (Cu_2FeS_4), $\leq$ 150 and $\geq$ 200 mesh
14	Reverbatory Matte (Noranda), $\leq$ 100 mesh
15	Reactor Matte (Noranda), $\leq$ 100 mesh
16	Converter White Metal (Noranda), $\leq$ 100 mesh

Table 2. Reagents

Material	Supplier	Grade
Sodium thiosulfate (pentahydrate)	Anachemia Chemicals Ltd.	technical
Potassium tetrathionate	Eastern Chemical	reagent
Sodium hydroxide	J. T. Baker Co.	reagent
Sulfuric acid (98%)	J. T. Baker Co.	reagent
Ferrous sulfate (heptahydrate)	J. T. Baker Co.	reagent
Zinc nitrate (hexahydrate)	J. T. Baker Co.	reagent
Lead (II) nitrate	J. T. Baker Co.	reagent
Silver nitrate	J. T. Baker Co.	reagent

3. GAS UPTAKE EXPERIMENTS

3.1 Screening of CANMET Ore Concentrates

Sixteen different copper containing sulfides, supplied by CANMET (Canada Centre for Mineral and Energy Technology), were assessed for catalytic activity towards thiosulfate oxidation by measuring their respective rates of oxygen uptake at constant temperature and pressure using the oxygen uptake apparatus described in the Experimental section. The relative activity of these catalysts, summarized in Table 3, was determined by comparing their initial rates of oxygen consumption for thiosulfate oxidation.

Catalysts 1 (Natural CuS), 2 (Synthetic CuS), 12 (Chalcopyrite) and 13 (Bornite) showed no activity towards thiosulfate oxidation.

Catalysts 5 and 7 (Synthetic Cu_2S), 11 (Copper Concentrate (Cu_2S + Ni_3S_2)), and 15 (Reactor Matte) exhibited moderate catalytic activity.

Catalysts 3 (White Metal), 4 (Copper Matte), 6 and 8 (both Synthetic Cu_2S), 9 and 10 (both Chalcocite Flotation Concentrates), 14 (Reverbatory Matte) and 16 (Converter White Metal) demonstrated the highest initial activity for thiosalt oxidation.

In order to identify the optimum operating parameters, two of the catalysts showing the greatest initial activity were chosen as the preferred copper sulfides for this study: ie. the Reverbatory Matte (catalyst 14) and the Converter White Metal (catalyst 16). Both of these materials, which were available in

Table 3. Relative activity of sulfides for thiosulfate oxidation. Conditions: T = 50°C; 5 mL distilled water; 0.200 g catalyst (4 (w/v) % catalyst loading); 0.100 g $Na_2S_2O_3.5H_2O$ (80 mM $S_2O_3^{=}$); 89.3 kPa oxygen partial pressure, shaking speed = 200 rpm.

Legend: ++ very active; + active; - no activity

Catalyst	Description	Relative Activity
1	Natural CuS (Covellite Crystals), $\leq$ 120 mesh	-
2	Synthetic CuS	-
3	White Metal from Hudson's Bay Mining and Smelting	++
4	Copper Matte (Cu-Fe-S), $\leq$ 100 mesh and $\geq$ 150 mesh	++
5	Synthetic Cu_2S, $\leq$ 325 mesh	+
6	Synthetic Cu_2S, $\leq$ 200 mesh	++
7	Synthetic Cu_2S, $\leq$ 150 mesh	+
8	Synthetic Cu_2S, $\geq$ 150 mesh	++
9	Chalcocite Flotation Concentrate, $\leq$ 325 mesh	++
10	Chalcocite Flotation Concentrate, $\geq$ 325 mesh	++
11	Copper Concentrate (Cu_2S + Ni_3S_2), $\leq$ 120 mesh	+
12	Chalcopyrite ($CuFeS_2$), $\geq$ 100 mesh	-
13	Bornite (Cu_2FeS_4), $\leq$ 150 mesh and $\geq$ 200 mesh	-
14	Reverbatory Matte from Noranda, $\leq$ 100 mesh	++
15	Reactor Matte from Noranda, $\leq$ 100 mesh	+
16	Converter White Metal from Noranda, $\leq$ 100 mesh	++

large quantities from Noranda, were analyzed and their respective elemental compositions are given in Table 4.

Table 4. Elemental Composition of Converter White Metal and Reverbatory Matte.

	wt. % Cu	wt. % Fe	wt. % S	wt. % other
Converter White Metal	80.1	0.7	15.0	4.2
Reverbatory Matte	33.5	12.8	27.2	26.5(1)

(1) consists mostly of SiO_2

3.2 Comprehensive Study of Preferred Thiosalt Oxidation Catalysts: Reverbatory Matte and Converter White Metal

3.2.1 Reproducibility and Representative Results

The reproducibility of oxygen uptake experiments for individual catalyst systems conducted under set experimental conditions was excellent. Typically, in duplicate or triplicate experiments, the various initial rates were within $\pm$ 3 % of each other for a given system, which is considered to be very good for kinetic experiments of this type.

Representative oxygen consumption curves for thiosulfate oxidation are shown in Figure 8 for the Reverbatory Matte and Converter White Metal catalysts.

The oxygen consumption curves in Figure 8 have an unusual shape ie. at some point, the oxygen consumption increases very rapidly. This can be explained if one remembers that the gas uptake apparatus is only capable of measuring the total oxygen being consumed by all thioanions in the system as well as the oxygen consumed due to the possible oxidative leaching of the

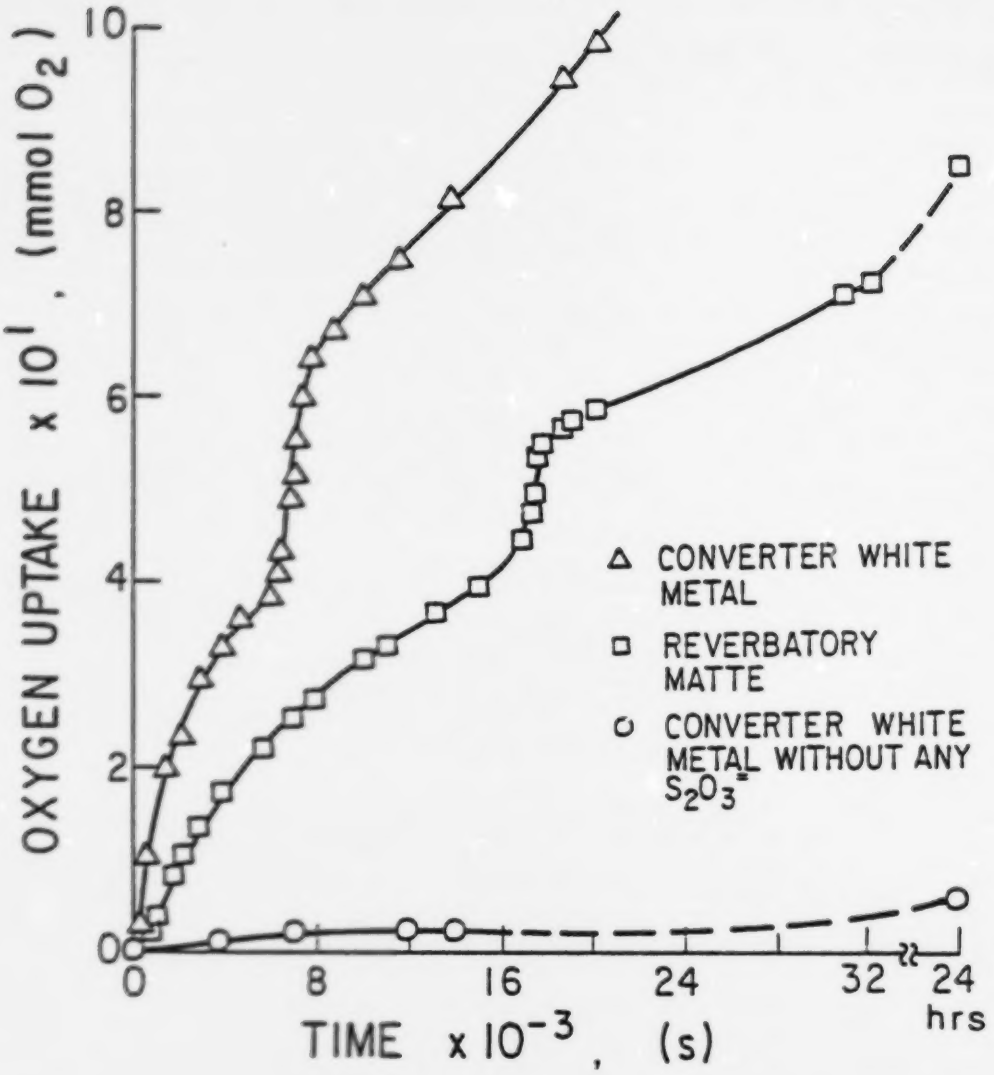


Figure 8. Representative oxygen uptake curves for Reverbatory Matte and Converter White Metal systems. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL distilled water; catalyst = 0.200 g (4 (w/v) % catalyst loading); $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^{=}$); d_p < 150 um; shaking speed = 200 rpm.

copper present in the ore concentrate.

$$S_2O_3^{=} + 2\ O_2 + H_2O \longrightarrow 2\ SO_4^{=} + 2\ H^+ \qquad (3.1)$$

$$2\ S_2O_3^{=} + 0.5\ O_2 + H_2O \longrightarrow S_4O_6^{=} + 2\ OH^- \qquad (3.2)$$

$$Cu + 0.5\ O_2 + 2\ H^+ \longrightarrow Cu^{2+} + H_2O \qquad (3.3)$$

$$Cu_2O + 0.5\ O_2 + 4\ H^+ \longrightarrow 2\ Cu^{2+} + 2\ H_2O \qquad (3.4)$$

$$Cu_2S + 0.5\ O_2 + 4\ H^+ \longrightarrow Cu^{2+} + CuS + 2\ H_2O \qquad (3.5)$$

These five reactions all consume O_2 and may contribute to the measured uptake. Reactions (3.1) and (3.2) will be discussed in greater detail in the Reaction Chemistry and Kinetics section (section 4.1.1); the implications of reactions (3.3), (3.4) and (3.5) are discussed in section 3.2.8.

An experiment conducted with the Converter White Metal in the presence of thiosulfate was stopped just as the O_2 consumption began to increase dramatically (see Figure 8). The resulting solution was analyzed and the product distribution at this instant as well as the results for a corresponding experiment conducted for a 24 hour period are presented in Table 5.

After 4900 seconds of reaction, only 1.38 mM $S_2O_3^{=}$ remains (initial $[S_2O_3^{=}]$ = 80 mM); most of the initial $S_2O_3^{=}$ appears to have been converted to $S_4O_6^{=}$ via reaction (3.2). Only trace amounts of $S_3O_6^{=}$ are evident. The thiosulfate and tetrathionate are oxidized to sulfate via reactions (3.1) and (3.6), respectively.

Table 5: Product distribution after indicated time period. (initial $[S_2O_3^{=}]$ = 80 mM; total initial sulfur = 160 mmol) (Refer to Figure 8).

Time	pH	$[S_2O_3^{=}]$ (mM)	$[S_3O_6^{=}]$ (mM)	$[S_4O_6^{=}]$ (mM)	$[SO_4^{=}]$ (mM)	Total S (mM)	$[Cu^{2+}]$ (ppm)
4900 s	2.28	1.38	0.09	8.22	66.0	101.9	2232
24 hrs	4.48	0	0	0	82.0	82.0	1573

$$S_4O_6^{=} + 7/2\ O_2 + 3\ H_2O \longrightarrow 4\ SO_4^{=} + 6\ H^{+} \qquad (3.6)$$

After 4900 seconds, the $SO_4^{=}$ concentration is 66.0 mM.

The pH is very acidic after 4900 seconds of reaction (ie. 2.28) since acid is produced during the major thioanion oxidation processes (see equations (3.1) and (3.6)). This acid is potentially capable of leaching some of the copper present in the ore concentrate, thus further contributing to the measured oxygen uptake and consequently capable of explaining the high copper values in solution (see section 3.2.8 for description of this leaching process). The Cu^{2+} thus formed (reactions (3.3), (3.4) and (3.5)) can react with the $SO_4^{=}$ in solution to produce basic copper sulfate precipitates (see section 4.1.3 and Appendix II for discussion on the formation of these precipitates) which undoubtedly are accountable for the poor sulfur mass balance (ie. only 64 % of total sulfur is accounted for after 4900 s of reaction).

After 24 hours of reaction, all $S_2O_3^{=}$, $S_3O_6^{=}$, and $S_4O_6^{=}$ have been oxidized to $SO_4^{=}$. The pH is less acidic than at 4900 seconds due to reactions (3.3), (3.4) and (3.5) which consume acid. The mass balance is even worse than before (ie. only 51 %

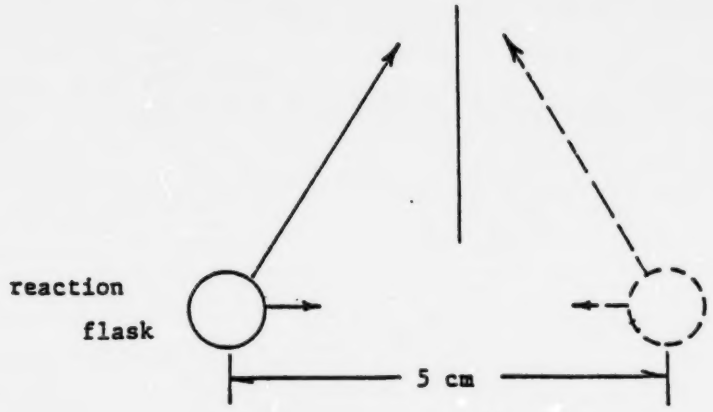
of total sulfur is accounted for) and the Cu^{2+} concentration is lower due to formation of the sulfate precipitates. The light blue copper sulfate precipitates mentioned above were evident in all experiments conducted with the Converter White Metal.

Also shown in Figure 8 is an experiment conducted with Converter White Metal in the absence of any $S_2O_3^=$. The uptake is due only to reactions (3.3) ,(3.4) and (3.5). During the thiosulfate oxidation process, acid is produced; since no thiosulfate is present in the system, the amount of leaching is limited (ie. leaching rate is directly proportional to the H^+ concentration as described in section 3.2.8).

The $O_2/S_2O_3^=$ molar ratio should be 2 for complete thiosulfate oxidation to sulfate (reaction (3.1)). Since 0.4 mmol $S_2O_3^=$ was present initially, the total O_2 uptake after 24 hours should be 0.8 mmol O_2. The ratio observed is approximately 2 for the Reverbatory Matte as expected since this ore concentrate contains only 33.5 % Cu (Table 4) and since this copper is not very susceptible to leaching. After 24 hours, no basic copper sulfates are evident for the Reverbatory Matte system. However, the ratio is much greater than 2 for the Converter White Metal system because it is probably more susceptible to leaching; also, it contains 80.1 % copper as shown in Table 4. The rate of copper leaching is thus greater contributing to the increased O_2 uptake. Therefore, although the initial rate of O_2 consumption is less for the Reverbatory Matte than for the Converter White Metal, it is a better "behaved" catalyst because its copper content is not as easily leached.

3.2.2 Effect of Shaking Speed

As discussed in the Experimental section, the reaction flask was clipped to a metal piston rod driven by a variable speed electric motor (ie. B in Figure 1). The speed of the motor, expressed in revolutions per minute (rpm), corresponds in a 1:1 ratio to the number of cycles the reaction flask makes in one minute. A single cycle is constituted by the 2 x 5 cm distance travelled by the flask as shown below (21).



Thus, a motor speed of 200 rpm (for example) corresponds to a shaking speed of 200 cycles per minute.

The effect of shaking speed on the initial rate of oxygen consumption was investigated at 175 rpm, 200 rpm, and 250 rpm. The initial rate (mmol O_2/s.g cat.) is plotted as a function of shaking speed in Figure 9.

When the shaking speed drops below 200 rpm, a rapid decrease in initial rate occurs due to the following two reasons:

a) At low shaking speeds, some settling of the catalyst occurs in the bottom of the reaction flask since the sulfides are very dense . Thus the slurry is no longer homogeneous and

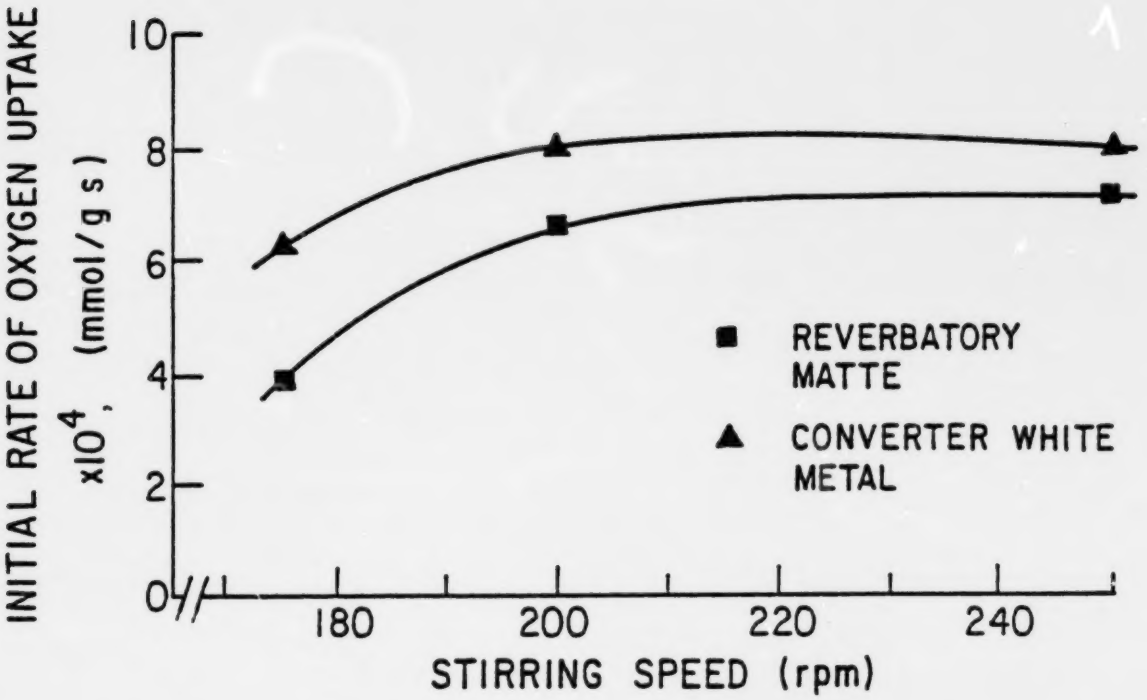


Figure 9. Effect of shaking speed on initial rate of oxygen uptake. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL distilled water; catalyst = 0.200 g (4 (w/v) % catalyst loading); $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^{=}$); d_p < 45 um.

the settled catalyst is not as effective since less surface area is exposed to the solution.

b) At low shaking speeds, the problem of mass transfer of the oxygen from the gas phase to the liquid phase becomes significant. The initial rate is limited by the amount of O_2 transferred into solution.

All subsequent gas uptake experiments were conducted at a shaking speed of 200 rpm to minimize the problem of oxygen mass transfer; this value was chosen since higher speeds might damage the fragile glass spiral coil connecting the reaction flask to the capillary manometer.

3.2.3 Effect of Catalyst Loading

Oxygen consumption experiments for thiosulfate oxidation in the presence of Reverbatory Matte and Converter White Metal were carried out for three different catalyst loadings (weight of catalyst per volume of solution): 2 (w/v) %, 4 (w/v) % and 8 (w/v) %. The kinetic results obtained are shown in Figure 10. In both cases, the absolute initial rate (not shown), which is expressed in mmol O_2 per second, increases non-linearly with catalyst loading. The initial rate, expressed as mmol O_2 per second per catalyst weight, decreases with loading. The decrease is more pronounced with the Converter White Metal system suggesting that O_2 mass transfer at the gas-liquid interface begins to control the rate at higher loadings. The mass transfer of O_2 to catalyst particles is extensively discussed by Satterfield (22).

As shown in Appendix IIIA, the data in Figure 10 can be

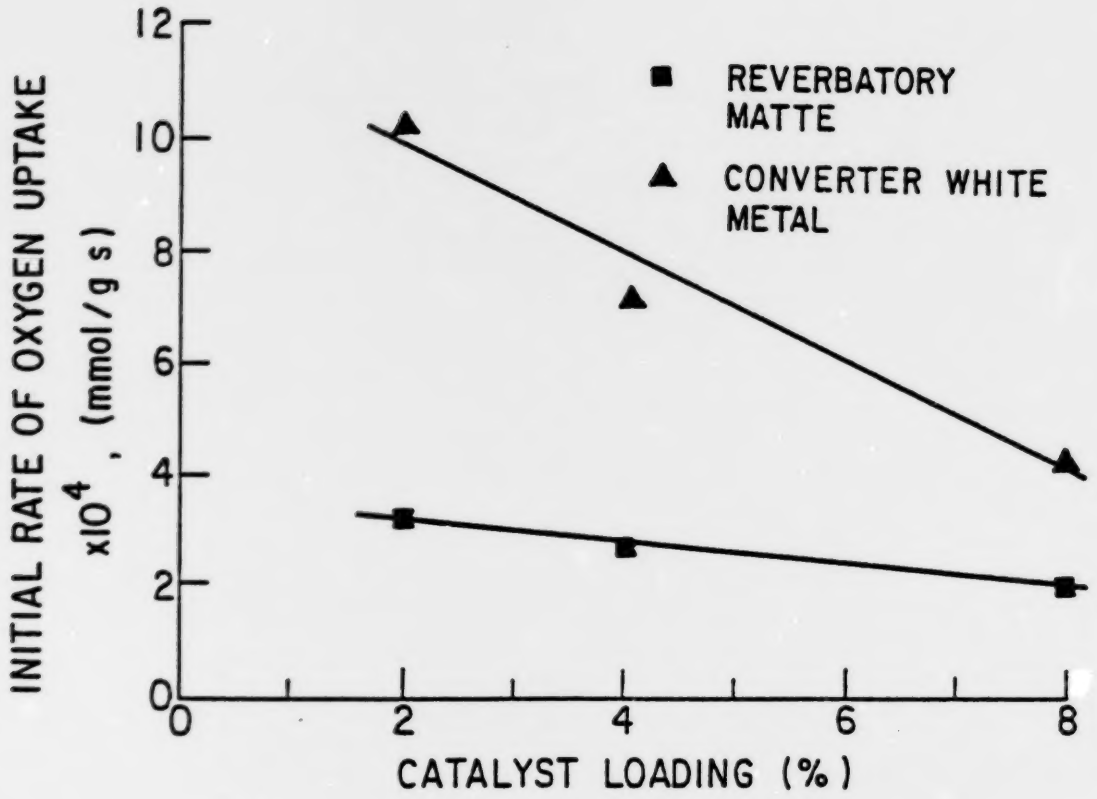


Figure 10. Effect of catalyst loading on initial rate of oxygen uptake. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^=$); d_p < 45 um; shaking speed = 200 rpm.

treated and plotted in inverse form to yield a straight line indicating that at high catalyst loadings and at a temperature of 50°C, the transfer of O_2 from the gas to the liquid begins to control the rate.

Mass transfer is not a problem in all gas experiments performed since only a 4 (w/v) % catalyst loading was used.

N.B.: It is very important to note that these calculations do not apply to the batch and slurry reactors subsequently used. The use of high loadings with these reactors (to be described in the Batch and Continuous Studies sections) would require a reevaluation of such mass transfer considerations.

3.2.4 Effect of Particle Size

Both the Reverbatory Matte and Converter White Metal materials were ground and then sieved; three size fractions were collected:

a) $d_p < 45\ \mu m$ ($d_p <$ 325 mesh)

b) $45\ \mu m < d_p < 125\ \mu m$ (325 mesh $< d_p <$ 120 mesh)

c) $125\ \mu m < d_p < 250\ \mu m$ (120 mesh $< d_p <$ 60 mesh)

The initial rate (mmol O_2/s.g cat.) is plotted as a function of particle diameter as shown in Figure 11. In both cases, the initial rate is seen to exhibit an inverse dependence on the particle diameter. This result is not surprising since coarser powders are less effective per unit mass because less catalyst surface area is exposed to the solution. In all subsequent oxygen uptake experiments, a particle size of less than 45 μm was used in order to provide the maximum possible initial rates of

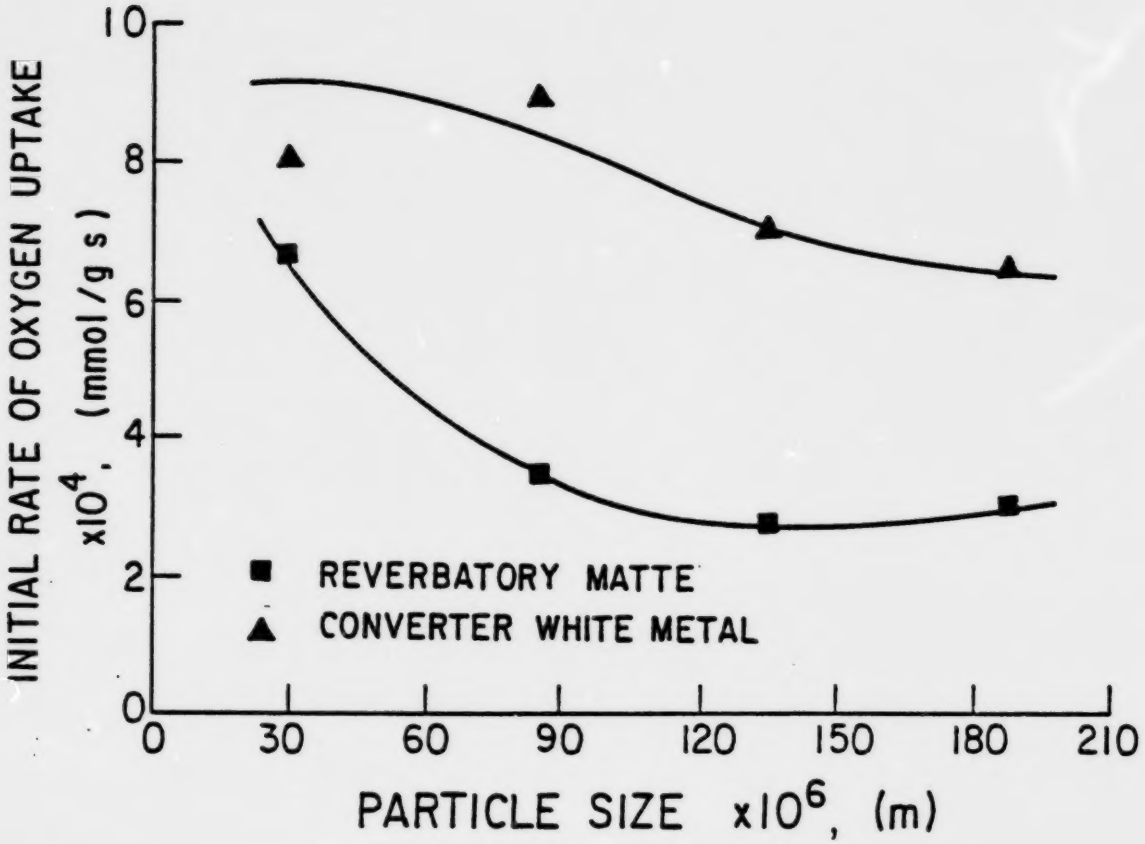


Figure 11. Effect of catalyst particle diameter on initial rate of oxygen uptake. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL distilled water; catalyst = 0.200 g (4 (w/v)% catalyst loading); $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^=$); shaking speed = 200 rpm.

oxygen consumption.

3.2.5 Effect of Oxygen Partial Pressure

In order to determine the effect of the oxygen partial pressure on the rate of oxidation of $S_2O_3^=$, the oxygen partial pressure was varied from 18.7 kPa to 97.3 kPa at 50°C. The oxygen partial pressure is determined as follows:

For experiments using pure oxygen:

$$P(O_2) = P_{total} - P(H_2O,T) \qquad (3.7)$$

where $P(O_2)$ = oxygen partial pressure

P_{total} = total pressure in system

$P(H_2O,T)$ = vapour pressure of H_2O at temperature T

For experiments using air:

$$P(O_2) = 0.209(P_{total} - P(H_2O,T)) \qquad (3.8)$$

where 0.209 = O_2 content by volume in air

As shown in Figure 12, the rate increases linearly with the oxygen partial pressure indicating that the overall rate of reaction is first order with respect to oxygen over the range investigated.

3.2.6 Effect of Temperature and Calculation of Overall Activation Energy

The catalyzed O_2 oxidation of thiosulfate was carried out at 40°C, 50°C and 60°C in order to determine the overall activation energy of the oxidation process for the Reverbatory Matte and Converter White Metal systems.

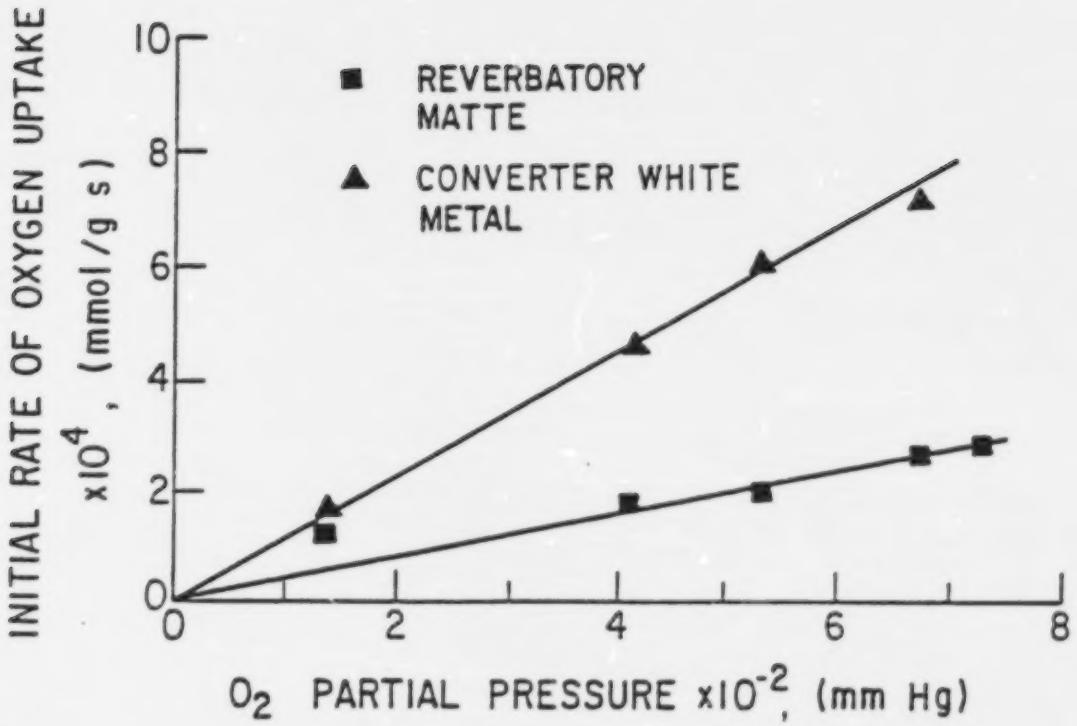


Figure 12. Effect of oxygen partial pressure on initial rate of oxygen uptake. Conditions: T = 50°C; 5 mL distilled water; catalyst = 0.200 g (4 (w/v) % catalyst loading); $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^{=}$); d_p < 45 um; shaking speed = 200 rpm.

The overall activation energy, E, may be calculated from the Arrhenius function shown in equation (3.9).

$$\ln k = -\left(\frac{E}{R}\right)\left(\frac{1}{T}\right) + \ln A \qquad (3.9)$$

If the experimental conditions are kept constant for each experiment, and since k is proportional to the initial rate, a plot of the natural logarithm of the initial rate versus 1/T should yield a straight line of slope -E/R. Such is the case for the catalyzed O_2 oxidation of thiosulfate, as shown in Figure 13.

The overall activation energies for the Reverbatory Matte and Converter White Metal catalyst systems are 29.0 kJ/mol O_2 (6920 cal/mol O_2) and 32.5 kJ/mol O_2 (7760 cal/mol O_2), respectively. These results signify that the reaction is relatively temperature-insensitive and that lower reaction temperatures could be used without significantly affecting the oxidation rate.

3.2.7 Effect of Initial Thiosulfate Concentration

The complete oxidation of thiosulfate to sulfate can be written as shown in equation (3.1). The corresponding rate expression can be expressed as in (3.10).

$$-\frac{d[S_2O_3^{=}]}{dt} = -\frac{1}{2}\left(\frac{d[O_2]}{dt}\right) = k'\,[S_2O_3^{=}]^n \qquad (3.10)$$

where k' = pseudo first order rate constant which comprises the catalyst concentration, the O_2 partial pressure, etc ...

n = order of reaction

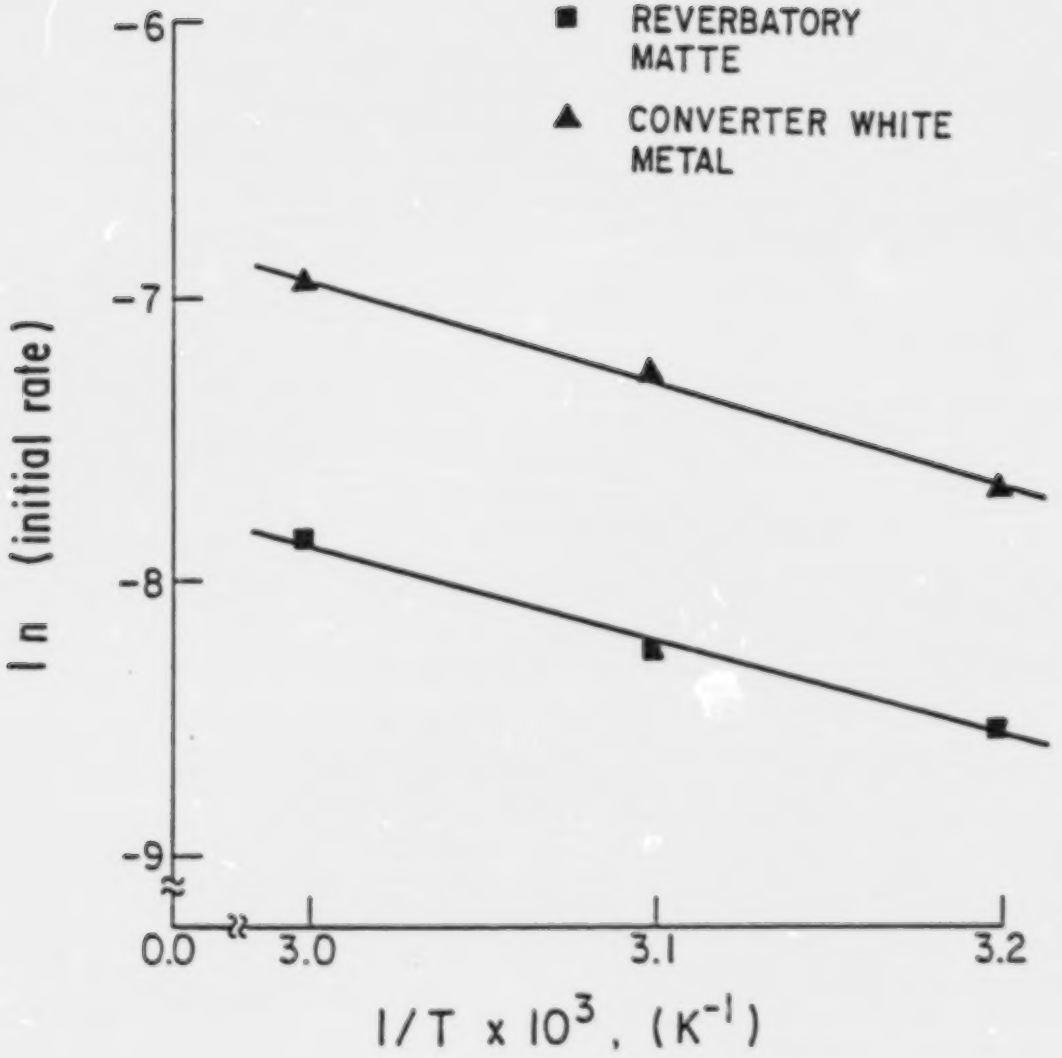


Figure 13. Arrhenius plot of initial rate of oxygen uptake for catalyzed oxygen oxidation of $S_2O_3^=$. Conditions: 89.3 kPa oxygen partial pressure; 5 mL distilled water; catalyst = 0.200 g (4 (w/v)% catalyst loading); $Na_2S_2O_3.5H_2O$ = 0.100 g (80 mM $S_2O_3^=$); d_p < 45 um; shaking speed = 200 rpm.

If the initial rate of O_2 uptake and the initial $S_2O_3^=$ concentration are substituted in equation (3.10), the relation can be written as shown by equation (3.11).

$$-\left(\frac{d[O_2]}{dt}\right)_{initial} = 2k'[S_2O_3^=]_{initial} \qquad (3.11)$$

A plot of the initial rate as a function of initial $S_2O_3^=$ concentration will yield a straight line of slope 2k' if n = 1. Such a plot is shown in Figure 14 thus suggesting a first order dependance on thiosulfate concentration. The pseudo-first order rate constants are given in Table 6 for both the Reverbatory Matte and the Converter White Metal systems under the experimental conditions outlined in Figure 14.

Table 6. Pseudo-first order rate constants for Reverbatory Matte and Converter White Metal systems (50°C).

Catalyst	Pseudo first order rate constant, k' (s^{-1})
Reverbatory Matte	1.216×10^{-6}
Converter White Metal	2.160×10^{-6}

Thus, at 50°C and under otherwise identical conditions, the Converter White Metal is 1.8 times more active than the Reverbatory Matte.

Also, it is of interest to note that the intercept of the plot presented in Figure 14 does not pass through zero since other reactions also consumes oxygen in the presence or absence of $S_2O_3^=$ ie. the oxidation of the copper present in the ore

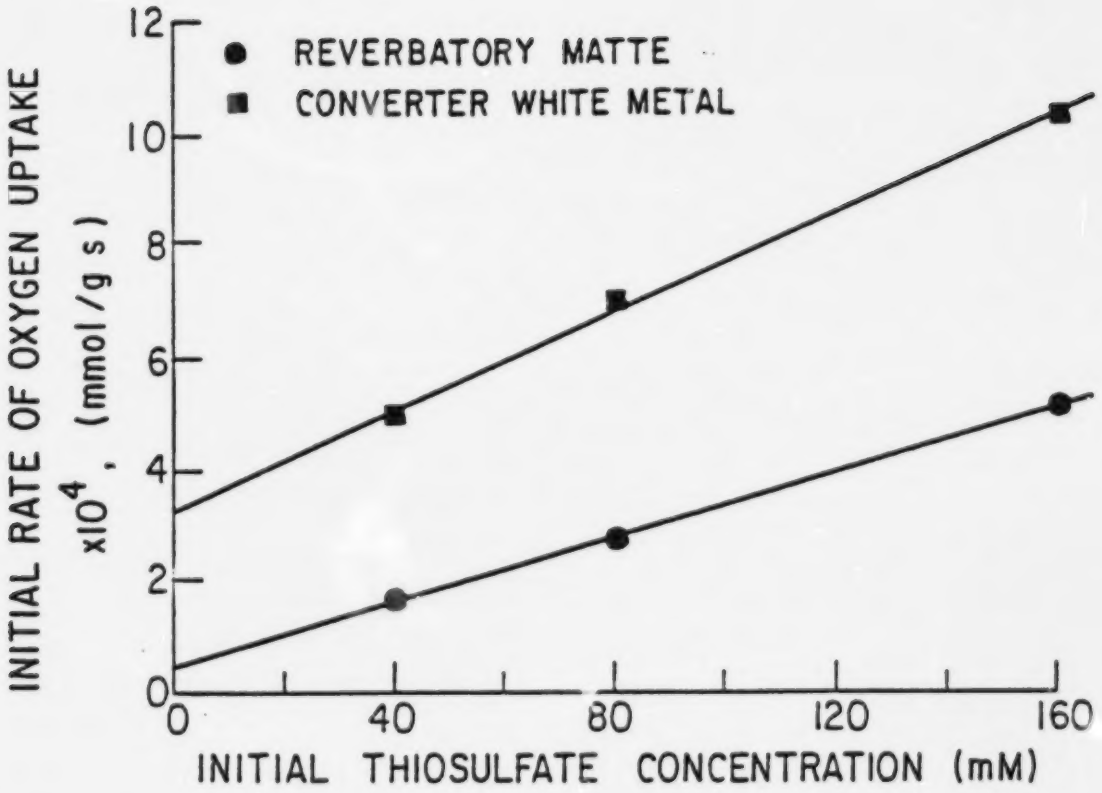


Figure 14. Effect of initial thiosulfate concentration on the initial rate of oxygen uptake. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL distilled water; catalyst = 0.200 g (4 (w/v) % catalyst loading); d_p < 45 um; shaking speed = 200 rpm.

concentrate (see sections 3.2.1 and 3.2.8). The intercept is almost zero for the Reverbatory Matte system since the copper present in this material is not very susceptible to oxidative leaching; however, the intercept is much larger for the Converter White Metal system indicating that this material is much more susceptible to oxidative leaching of the copper present in the ore concentrate (see section 3.2.8).

3.2.8 Effect of pH on the Catalyst

During the oxidation of thiosulfate, both sulfate and acid are produced as shown in equation (3.1). The acid produced in the thiosulfate oxidation process has the potential to react with the reduced copper (ie. metallic copper or Cu(I)) present in the catalyst to form Cu^{2+} in the presence of oxygen (reactions (3.3), (3.4) or (3.5)).

Various H_2SO_4/H_2O buffers (pH of 5.60, 2.42, 2.01, 1.48 and 0.96) were used as the reaction medium in the absence of thiosulfate in order to observe the stability of the catalyst, with respect to oxidation, as a function of pH. Consequently, any O_2 consumed would be due to the leaching process shown in reactions (3.3), (3.4) and (3.5).

The results of this study, which are presented in Figure 15, clearly show that above a pH of about 3, only a relatively small amount of leaching occurs. However, if the pH of the reaction medium drops below 2 considerable oxidation of the catalyst takes place.

These observations can be explained as follows:

a) At low temperatures and using O_2 as the oxidizing agent,

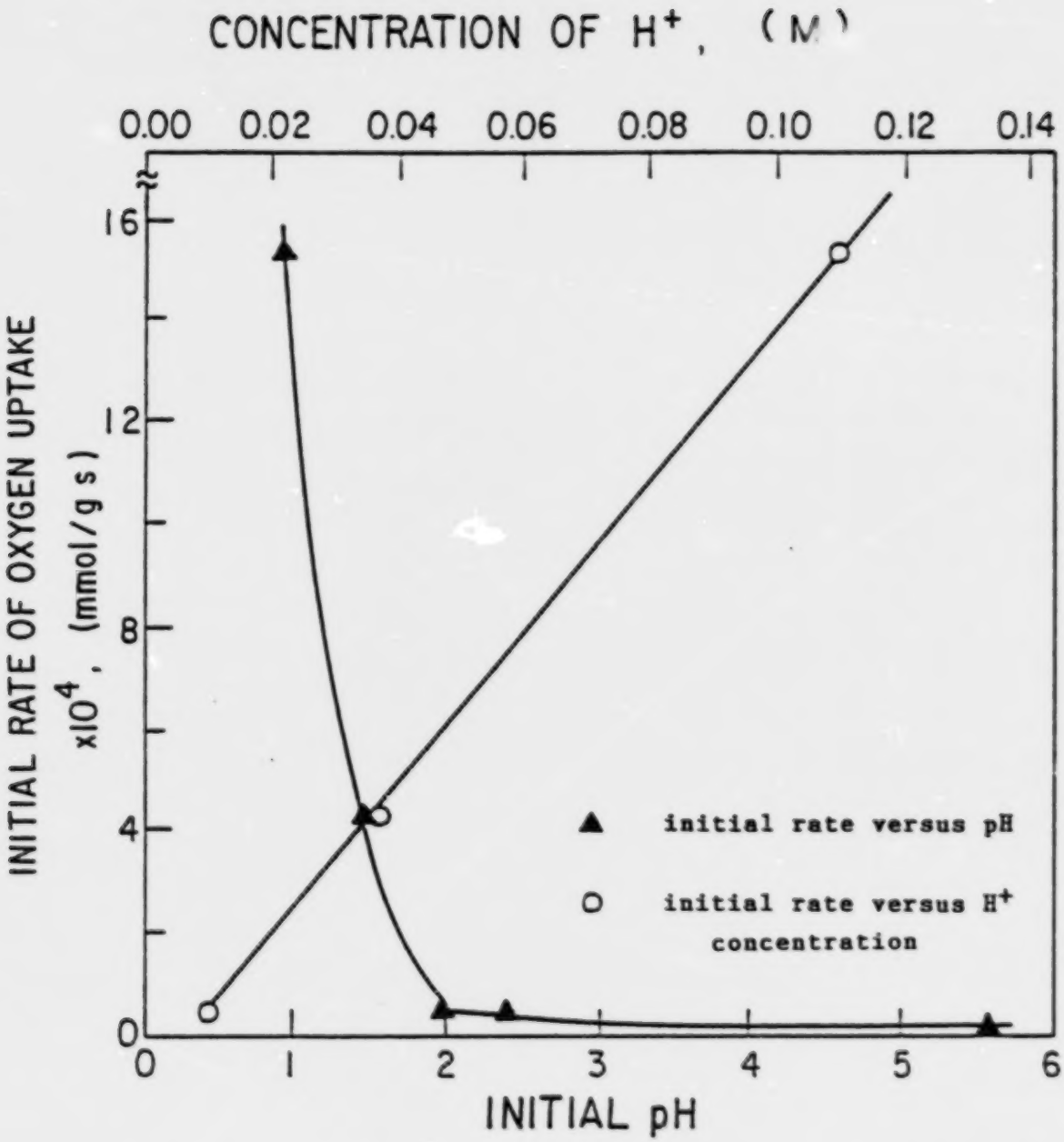


Figure 15. Effect of initial pH and H^+ concentration on the stability of the Converter White Metal with respect to oxidation. Conditions: T = 50°C; 89.3 kPa oxygen partial pressure; 5 mL H_2SO_4/H_2O buffer; catalyst = 0.200 g (4 (w/v) % catalyst loading); d_p < 45 um; shaking speed = 200 rpm.

the leaching occurs in a two stage process as extensively described by Gomez-Bueno for the Cu_2S system (23). The first step products are covellite (CuS) and copper ions whereas the second step products are elemental sulfur and copper ions. The second stage is not observed in our system and will not be discussed.

b) The three reactions observed in the first stage are: (i) oxygen adsorption on certain surface sites, (ii) protonation of adsorbed species, and (iii) migration of Cu^+ ions from the Cu_2S crystal lattice to the surface where it is oxidized to Cu^{2+}. These three reactions are given in Scheme 1 (reactions (3.12) to (3.16), inclusively). The apparent activation energy of the first stage dissolution process was found to be 28.5 kJ/mol (6800 cal/mol) (23).

The dissolution process for Cu_2S is schematically illustrated in Figure 16 (24). The first stage leaching rate for the Cu_2S dissolution process can be represented by an adsorption isotherm type relationship (equation (3.17)).

$$\frac{d[Cu^{2+}]}{dt} = \frac{A[H^+]}{1 + B[H^+]} [O_2] \qquad (3.17)$$

where A and B are constants (at a given temperature) dependent on the catalyst system under study

Since $d[Cu^{2+}]/dt = -2d[O_2]/dt$ (refer to equation (3.3)), equation (3.17) can be written as:

$$-\frac{d[O_2]}{dt} = \frac{A[H^+]}{2(1 + B[H^+])} [O_2] \qquad (3.18)$$

Scheme 1. First stage leaching process for Cu_2S system (23)

Adsorption of O_2 on the mineral surface

$$Cu_2S \diagup + O_2\,(aq) \longrightarrow Cu_{2-x}S \diagup Cu^+ \text{---} O_2 \qquad (3.12)$$

(The symbol $\diagup$ is used to denote a surface site)

Protonation of the adsorbed site

$$Cu_{2-x}S \diagup Cu^+ \text{---} O_2 + H^+ \longrightarrow Cu_2S\ Cu_{2-x}S \diagup Cu^+ \text{--} HO_2 + Cu^{2+} \qquad (3.13)$$

Protonation of an already protonated site

$$Cu_2S\ Cu_{2-x}S \diagup Cu^+ \text{--} HO_2 + H^+ \longrightarrow Cu_2S\ CuS\ Cu_{2-x}S \diagup Cu^+ \text{--} H_2O_2 + Cu^{2+} \qquad (3.14)$$

By further protonation of the same site

$$Cu_2S\ CuS\ Cu_{2-x}S \diagup Cu^+ \text{--} H_2O_2 + H^+ \longrightarrow Cu_2S\ CuS\ CuS\ Cu_{2-x}S \diagup Cu^+ \text{--} OH + H_2O + Cu^{2+} \qquad (3.15)$$

By further protonation of the same site

$$Cu_2S\ \ CuS\ CuS\ Cu_{2-x}S \diagup Cu^+ \text{--} OH + H^+ \longrightarrow Cu_2S\ CuS\ CuS\ CuS\ Cu_{2-x}S \diagup Cu^+ + H_2O + Cu^{2+} \qquad (3.16)$$

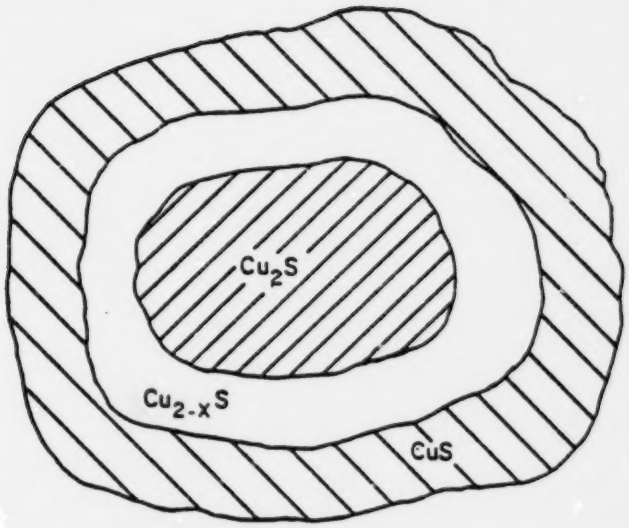


Figure 16. Leaching of Cu_2S particle with oxygenated sulfuric acid solution at low temperature and pressure: first stage leaching. (24)

For the Cu_2S system investigated by Gomez-Bueno, A is much greater than B; therefore, at low H^+ concentrations (ie. $[H^+] < 1.0$ M), the denominator $1 + B[H^+]$ can be taken as unity and equation (3.18) can be written as shown in (3.19).

$$-\frac{d[O_2]}{dt} = k' [H^+] [O_2] \qquad (3.19)$$

This relationship indicates that the leaching rate shows a pseudo-first order relationship with the H^+ and O_2 concentrations when $[H^+] < 1$ M.

Since the Cu_2S leaching process is similar to that for the Converter White Metal material (ie. Converter White Metal consists mostly of Cu_2S), these findings also apply to this study. Figure 15 also shows a plot of the initial rate of oxygen uptake as a function of the H^+ concentration (for $[H^+]$ of 0.1096 M, 0.0333M and 0.0098M). The linear nature of this plot indicates that the relationship expressed in equation (3.19) applies to our system when the H^+ concentration is less than 1 M. The value for $k' [O_2]$ was found to be 5.03×10^5 mol/(g hr).

In conclusion, the pH of the reaction medium has a pronounced effect on the copper leaching rate. The results shown in Figure 15 indicate that a reaction medium pH greater than 4 will minimize the amount of copper leached into solution.

3.2.9 Use of Acetate and Phosphate Buffers as Reaction Medium

Since acid is produced during the thiosalt oxidation process, the pH of the slurry decreases steadily with time thereby increasing the rate of leaching of copper into solution

(ie. first order dependance of rate on H^+ concentration as discussed in section 3.2.8). To keep the pH constant throughout the experiment, two different buffers were investigated as the reaction medium.

a) pH 4.52 Acetate Buffer

The preparation of this NaAc/HAc buffer is described in (25). The use of this buffer caused considerable leaching of the copper present in the catalyst probably due to the complexing of Cu^{2+} by acetate ligands. The solution was dark blue in colour; also, a greenish precipitate was evident along the edges of the reaction flask indicating the presence of copper acetate.

b) pH 6.4 phosphate buffer

The preparation of this buffer is also described in (25). The buffer demonstrated good buffering capability. However, no further work was carried out with this phosphate buffer since the use of such a buffering system would not be practical for a continuous process.

3.2.10 Reuse of Catalyst

In order to determine if the catalysts' activity diminishes with use, both the Reverbatory Matte and the Converter White Metal were investigated for reuse. Before being used a second time, the catalysts were washed three times with distilled water and allowed to dry overnight in a dessicator.

The Reverbatory Matte showed a slight decrease in initial rate whereas the Converter White Metal showed no decrease at all in its activity for $S_2O_3^=$ oxidation in the presence of O_2. Also,

in both cases the soluble copper values in solution were much lower after a period of 24 hours indicating that most of the easily leached copper was removed during the first use of the catalyst materials. Therefore, it appears that the activity of the catalyst does not decrease significantly over a couple of days of use.

4. BATCH EXPERIMENTS

In order to get a better understanding of the catalyzed oxidation of thiosalts, various batch experiments were carried out to obtain product distributions as a function of time. Mass transfer calculations for the batch reactor employed in these studies are shown in Appendix IIIB.

Although some work was performed on a few of the other very active catalysts shown in Table 3, the bulk of the batch experiments was done with the two preferred catalysts identified in the gas uptake screening process: ie. the Reverbatory Matte and the Converter White Metal, both supplied by Noranda.

4.1 Preliminary Investigations Using Synthetic Effluent Consisting of Sodium Thiosulfate

In this series of batch experiments, the test effluent solution contained sodium thiosulfate as the thioanion substrate.

A particle diameter of 45 μm to 125 μm was chosen for all batch experiments since, as discussed by Satterfield (22), the preferred size of catalysts for slurry reactors is typically about 75 to 200 μm in diameter. Finer powders (ie. $d_p < 75$ μm) are more difficult to remove by settling or filtration; coarser powders (ie. $d_p > 200$ μm) are more difficult to suspend and may be less effective per unit mass since less catalyst surface area is exposed to the solution.

4.1.1 Reaction Chemistry and Kinetics

Reaction Chemistry

The aqueous chemistry of thiosalts is extensively discussed in CANMET Report 82-4E (2). Generally, polythionates can be oxidized either by hydrolysis (ie. water, protons or hydroxide ions are the attacking agents) or by nucleophilic degradation (ie. sulfite, thiosulfate or other nucleophilic species are the attacking agents) or by a combination of both.

A typical product distribution profile, obtained for thiosulfate oxidation in the presence of Converter White Metal at 40°C, is shown in Figure 17. The information contained in such a reaction profile is quite useful in postulating a possible reaction scheme for the oxidation of thiosulfate in the presence of air.

Initially, the $S_2O_3^=$ can be oxidized to form either $S_4O_6^=$ or $SO_4^=$ according to equations (4.1) and (4.2), respectively (30).

$$2\ S_2O_3^= + 0.5\ O_2 + H_2O \xrightarrow{k_1} S_4O_6^= + 2\ OH^- \qquad (4.1)$$

$$S_2O_3^= + 2\ O_2 + H_2O \xrightarrow{k_2} 2\ SO_4^= + 2\ H^+ \qquad (4.2)$$

Reaction (4.1) is favoured since it is the most facile route for oxidation (especially if oxygen transport or adsorption is limited) (see Kinetics discussion). If pathway (4.1) is favoured, the pH would initially be expected to increase. Under such basic conditions, $S_4O_6^=$ is unstable and would probably undergo decomposition to $S_2O_3^=$ and $S_3O_6^=$ (31) according to equation (4.3).

$$4\ S_4O_6^= + 6\ OH^- \xrightarrow{k_3} 5\ S_2O_3^= + 2\ S_3O_6^= + 3\ H_2O \qquad (4.3)$$

The thiosulfate and trithionate produced in reaction (4.3) can be

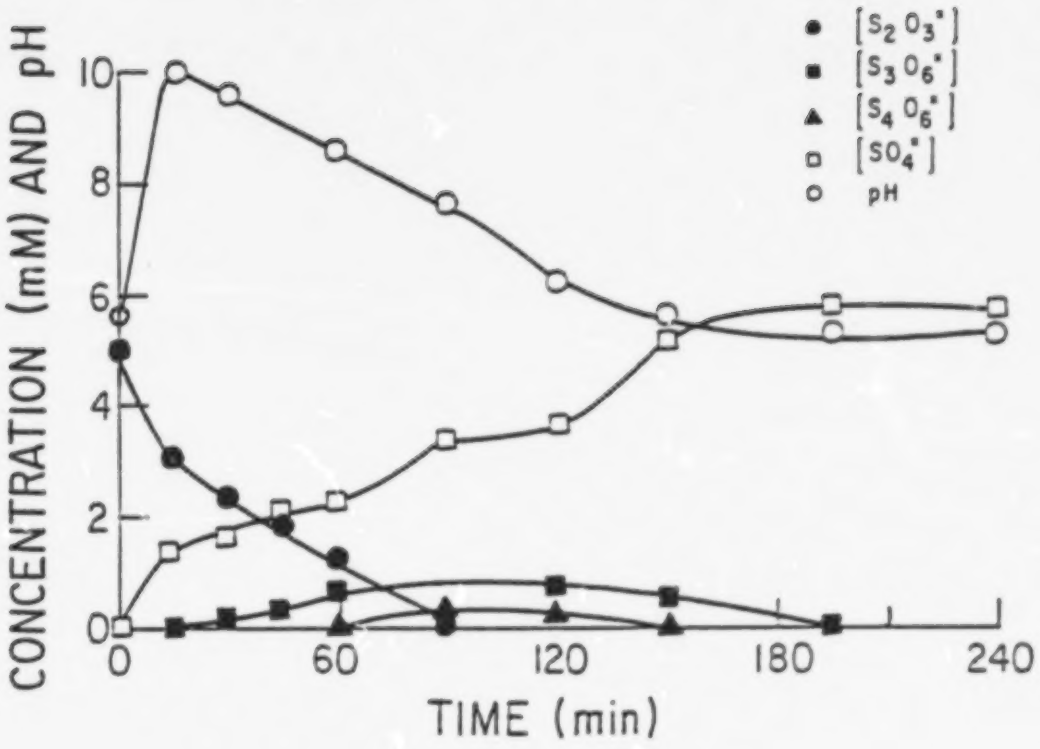


Figure 17. Representative product distribution profile for the Converter White Metal system. Conditions: T = 40°C; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0 mM $S_2O_3^=$); Converter White Metal = 32 g (8 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

oxidized to sulfate via reactions (4.2) and (4.6), respectively. Thus the complete oxidation of $S_4O_6^=$ to $SO_4^=$ can be written as in equation (4.4).

$$S_4O_6^= + 7/2\ O_2 + 3\ H_2O \xrightarrow{k_4} 4\ SO_4^= + 6\ H^+ \qquad (4.4)$$

These reactions help to explain four peculiarities shown in Figure 17.

a) The sharp increase in pH during the first 10 minutes is attributed to reaction (4.1). The slow decrease in pH after 10 minutes is likely due to reactions (4.2), (4.3) and (4.4).

b) Since reaction (4.3) is known to occur quite readily under basic conditions (31), no $S_4O_6^=$ is seen initially (ie. any $S_4O_6^=$ which is formed is quickly transformed to $S_2O_3^=$ and $S_3O_6^=$). In this regard, it is of interest to note that some $S_3O_6^=$ is evident after about 15 minutes of reaction.

c) The abnormal shape of the $S_2O_3^=$ curve can also be understood in terms of the chemistry presented above. At first, the decrease in $S_2O_3^=$ concentration is rapid but then slows down due to reaction (4.3) whereby $S_2O_3^=$ is reformed.

d) After about 90 minutes of reaction, the pH is no longer on the alkaline side. Under neutral or acidic conditions, the rate of reaction (4.3) becomes negligible explaining the appearance and accumulation of $S_4O_6^=$ at this point.

Under neutral or acidic conditions, the $S_3O_6^=$ produced in reaction (4.3) is known to hydrolyze to give thiosulfate, sulfate and acid (32) as shown in equation (4.5).

$$S_3O_6^= + H_2O \xrightarrow{k_5} S_2O_3^= + SO_4^= + 2\ H^+ \qquad (4.5)$$

The $S_2O_3^=$ produced in reaction (4.5) decomposes as in (4.2) to form $SO_4^=$. The overall $S_3O_6^=$ oxidation reaction can thus be expressed as shown in equation (4.6).

$$S_3O_6^= + 2\ O_2 + 2\ H_2O \xrightarrow{k_6} 3\ SO_4^= + 4\ H^+ \qquad (4.6)$$

The above reaction explains the rapid increase in sulfate concentration and decrease in pH at this point (ie. t = 120 minutes in Figure 17). Since trithionate is not easily directly oxidized to sulfate, it seems that the present catalyst system apparently gets around this problem by first decomposing $S_3O_6^=$ to $S_2O_3^=$ and $SO_4^=$. This is then followed by the oxidation of the adsorbed $S_2O_3^=$.

Further insight into the reaction chemistry of thiosalt oxidation can be obtained by conducting a series of oxidation experiments under anaerobic conditions. These investigations can provide an indication of the chemical intermediates and pathways involved in the oxidation of a specific thioanion. The results of such experiments, conducted under a nitrogen atmosphere with 10.0 mM $S_2O_3^=$, 9.6 mM $S_3O_6^=$ and 10.9 mM $S_4O_6^=$ solutions in the presence or absence of Converter White Metal catalyst, are shown in Table 7. These extremely interesting results can further help clarify the aerobic reaction chemistry discussed above.

a) 10.0 mM $S_2O_3^=$ solution: In the absence of any Converter White Metal catalyst, the thiosulfate solution remains very stable under anaerobic conditions. The pH remained relatively constant throughout the experiment since no acid was produced.

Table 7. Stabilities of 10 mM thiosalt solutions with and without Converter White Metal catalyst under anaerobic conditions over 120 hrs.

Conditions : 200 mL of 5 w/v % slurry in 250 mL Erlenmeyer flask, continuous stirring, sealed under N_2 atmosphere at ambient temperature (25°C).

sample		time (hrs)		$[S_2O_3^{=}]$ (mM)	$[S_3O_6^{=}]$ (mM)	$[S_4O_6^{=}]$ (mM)	$[SO_4^{=}]$ (mM)	total S (mM)	pH
$S_2O_3^{=}$ sol'n	no catalyst	0	(1)	10.0	0	0.5	0	22.0	-
		48		10.0	0	0.4	0	21.6	7.5
		120		10.1	0.3	0	0	21.1	8.6
	catalyst added	0		10.0	0	0.5	0	22.0	9.8
		3		7.9	2.6	0	0.6	24.2	10.5
		24	(2)	8.5	1.3	0	1.6	22.5	10.5
		48		0.2	0	0	6.4	6.8	2.9
$S_3O_6^{=}$ sol'n	no catalyst	0	(1)	0	9.6	0.1	0.6	29.8	-
		48		0.5	9.0	0.2	1.6	30.4	2.9
		120		1.4	7.9	0.2	2.2	29.5	2.4
	catalyst added	0		0	9.6	0.1	0.6	29.8	6.2
		3		0.2	9.5	0.3	0.8	30.9	6.4
		24	(3)	0	0	0.1	17.6	18.0	2.8
		48		0	0	0	17.2	17.2	3.3
$S_4O_6^{=}$ sol'n	no catalyst	0	(1)	0	0	10.9	0	43.6	-
		48	(4)	0.1	0	11.0	3.4	47.6	7.3
		120		0	0	10.4	0	41.6	5.7
	catalyst added	0		0	0	10.9	0	43.6	6.3
		3		0	0.2	9.5	1.0	39.6	6.0
		24		0	0	10.9	2.4	46.0	5.3
		48		0	0	6.0	9.0	33.0	3.9
H_2O only	catalyst added	0		0	0	0	0	0	6.5
		3	(4)	0	0	0.7	0.6	3.6	5.8
		24		0	0	0	0	0	5.0
		48		0	0	0	0	0	5.6

Notes: 1. pH approximately 6 at time = 0 hrs when no catalyst present

2. 1 M H_2SO_4 added to bring pH down to 6.5 after 24 hrs

3. copper "mirror" observed on inside of flask

4. sample possibly contaminated

However, in the presence of the Converter White Metal catalyst, the thiosulfate is slowly oxidized under basic conditions to sulfate via a tetrathionate intermediate (30) as shown in equation (4.7).

$$2\ S_2O_3^{=} + 2\ Cu^{2+} \longrightarrow S_4O_6^{=} + 2\ Cu^{+} \qquad (4.7)$$

This reaction requires the presence of Cu^{2+}, which is obtained from the dissolution of the catalyst (see section 3.2.8), in order to proceed explaining why the thiosulfate is not oxidized in the absence of catalyst. The tetrathionate thus formed can quickly decompose under basic conditions, as in equation (4.3), to thiosulfate and trithionate. Evidence for this pathway includes the appearance of $S_3O_6^{=}$ after 3 hours of reaction and the increase in $S_2O_3^{=}$ concentration observed after 24 hours. At this time, 1 M H_2SO_4 was added to the slurry to decrease the reaction medium pH from 10.5 to 6.5. This greatly enhanced the rate of formation of sulfate since the acidic medium accelerates the rate of oxidation of $S_3O_6^{=}$ produced in the oxidation of $S_4O_6^{=}$ (see part b)). The poor sulfur mass balance observed after 48 hours of reaction can be explained by the formation of copper sulfate precipitates (see section 4.1.3).

b) 9.6 mM $S_3O_6^{=}$ solution: When no catalyst is present in the system, the trithionate is very slowly oxidized, under acidic conditions, to thiosulfate and sulfate via reaction (4.5) which does not require the presence of oxygen. The $S_2O_3^{=}$ thus produced is stable and will not be oxidized under anaerobic conditions in the absence of catalyst as evidenced by the results discussed in part a). The pH decreases from approximately 6 to 2.4 over the

course of the experiment due to the acid produced in reaction (4.5). After 120 hours of reaction, the sulfur mass balance is excellent.

In the presence of the Converter White Metal catalyst, the trithionate solution is rapidly oxidized to sulfate and thiosulfate in less than 24 hours via the hydrolysis pathway given in equation (4.5). Contrasting this observation with the results obtained in the absence of catalyst indicates that the rate of reaction (4.5) is greatly enhanced by the presence of Converter White Metal under acidic conditions (ie. pH < 7). This fact is very important since only reaction (4.5) results in the direct production of sulfate (ie. all other reactions discussed above only result in the production of intermediates which are ultimately oxidized to trithionate); thus, the rate of formation of sulfate is limited by the rate at which trithionate is oxidized. Under anaerobic conditions, the Cu^{+} produced in reaction (4.7) can disproportionate to Cu^{0} (metallic copper) and Cu^{2+} (33) explaining the appearance of a copper mirror along the edges of the flask after 24 hours of reaction. The Cu^{2+} ions can react with the sulfate in solution to form sulfate precipitates explaining the poor sulfur mass balance observed after 48 hours of reaction (see section 4.1.3).

c) 10.9 mM $S_4O_6^{=}$ solution: Under essentially neutral conditions and in the absence of catalyst, the tetrathionate solution remained stable over a period of 120 hours. This indicates that the reaction shown in equation (4.3) requires the presence of Converter White Metal catalyst in order to proceed.

In the presence of Converter White Metal, the tetrathionate is slowly oxidized to sulfate under slightly acidic conditions. The rate of reaction is rather slow since reaction (4.3) is not very facile when the pH is less than 7. The relatively small amounts of trithionate and thiosulfate produced in this manner are quickly oxidized under acidic conditions to sulfate and thiosulfate, and tetrathionate, respectively, explaining the increase in tetrathionate concentration witnessed after 24 hours of reaction.

d) H_2O only: As expected, a solution containing only water in the presence of Converter White Metal did not contain any thiospecies.

In conclusion, the above discussion indicates that the complete oxidation of all thioanions to sulfate occurs via a variety of chemical pathways. The rates of these major pathways are influenced by such factors as the availability of reagents (eg. hydroxide ions), the presence of Converter White Metal catalyst and pH. Thus, under anaerobic conditions and in the absence of catalyst, the oxidation of $S_2O_3^=$, $S_4O_6^=$ and $S_3O_6^=$ is very slow; the presence of Converter White Metal catalyst is required to significantly enhance the oxidation rates.

Kinetic Study of the Converter White Metal Catalyst System

On the basis of the product distribution patterns shown in Figures 18 a to 18 d (at 30°C, 40°C, 50°C, and 60°C, respectively), the general kinetic features of the oxidation of thiosulfate can be studied. It should be noted that it is rather difficult to carry out a thorough kinetic study of this system

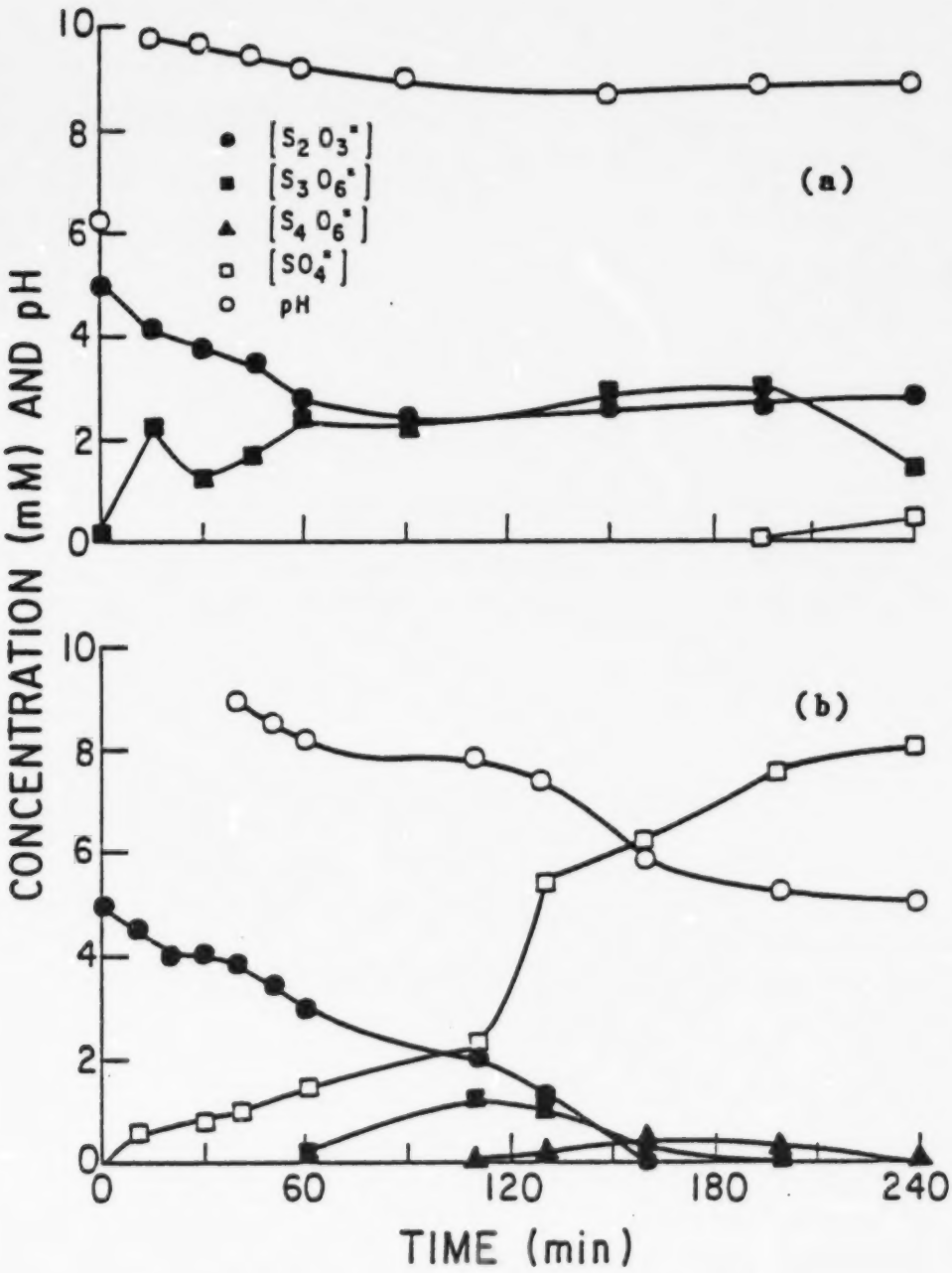


Figure 18. Effect of temperature on thiosalt oxidation rates: (a) 30°C, (b) 40°C, (c) 50°C, and (d) 60°C. Conditions: 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0mM $S_2O_3^=$); Converter White Metal = 16 g (4(w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

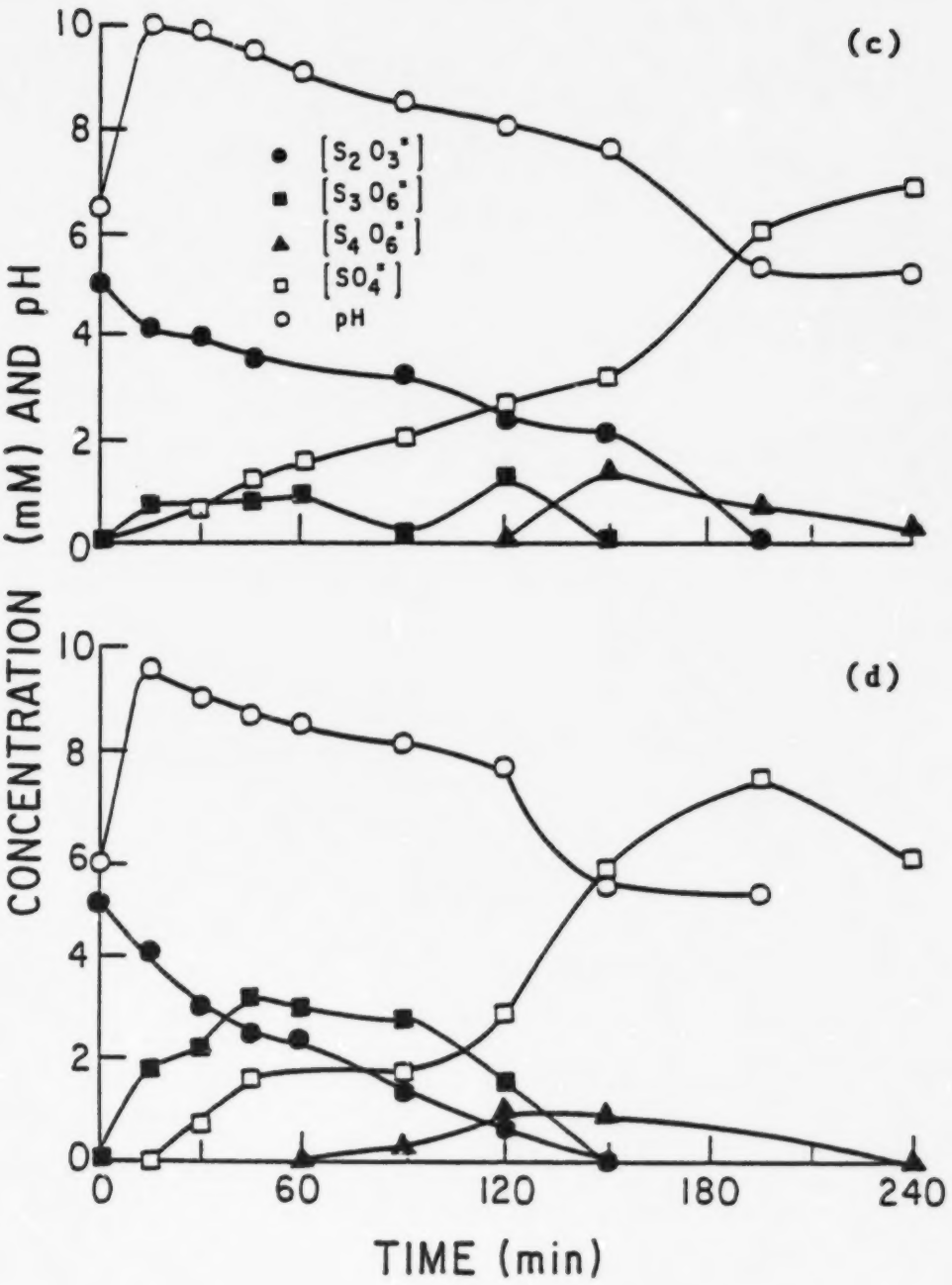


Figure 18. Effect of temperature on thiosalt oxidation rates: (a) 30°C, (b) 40°C, (c) 50°C, and (d) 60°C. Conditions: 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0mM $S_2O_3^=$); Converter White Metal = 16 g (4(w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

due to the multitude and complexity of the reactions (see Reaction Chemistry above). The method used to determine the rate expressions and rate constants for the various oxidation processes is similar to the one previously described by Chanda and Rempel (11).

The pseudo-homogeneous first order rate expressions for reactions (4.1), (4.2), (4.3) and (4.5) and the calculations for the Converter White Metal system are given in Appendix IV.

The rate constants and activation energies for oxidation of the various thiospecies in the presence of Converter White Metal (reactions (4.1), (4.2), (4.3) and (4.5)) are tabulated in Tables 8 and 9, respectively.

Table 8. Summary of Kinetic Data for Thioanion Oxidation in the Presence of Converter White Metal: Rate Constants.

Temp. (^{o}C)	$k_1 \times 10^3$ (min.$^{-1}$)	$k_2 \times 10^3$ (min.$^{-1}$)	$k_3 \times 10^2$ (min.$^{-1}$)	$k_5 \times 10^2$ (min.$^{-1}$)
30	6.51	0.889	----	1.75
40	4.64	2.00	1.51	2.76
50	4.89	2.22	1.92	----
60	9.99	5.33	3.45	5.93

Table 9. Summary of Kinetic Data for Thioanion Oxidation in the Presence of Converter White Metal: Activation Energies.

k	E (kJ/mol)	E (kcal/mol)
k_1	43.6	10.4
k_2	49.7	11.9
k_3	36.1	8.6
k_5	34.2	8.2

N.B.: k_3 (ie. oxidation of tetrathionate to thiosulfate and trithionate) and k_5 (ie. oxidation of trithionate to thiosulfate and sulfate) are not true rate constants but rather a combination of two or more rate constants. For example, k_3 comprises the rate constant for the decomposition of tetrathionate to thiosulfate and trithionate (reaction (4.3)) as well as the rate constants for the oxidation of the thiosulfate (via reactions (4.1) and/or (4.2)) and the trithionate (via reaction (4.5)). Similarly, k_5 is a combination of the rate constant for the decomposition of trithionate to thiosulfate and sulfate (reaction (4.5)) as well as the rate constant for the oxidation of the thiosulfate via reactions (4.1) and/or (4.2). The value of k_4 and k_6 cannot be determined by the method described by Chanda and Rempel (11).

As expected from the Reaction Chemistry discussion, k_1 (oxidation of thiosulfate to tetrathionate) is larger than k_2 (oxidation of thiosulfate to sulfate) by a factor of about two since the formation of tetrathionate is kinetically favoured. The catalyzed oxidation of trithionate to thiosulfate and sulfate under acidic conditions is very facile as evidenced by the large k_5 rate constants.

The kinetic results for the oxidation of $S_4O_6^{=}$ are rather difficult to explain in light of the preliminary Reaction Chemistry results; k_4 would be expected to be much smaller than both k_1 and k_2 since the catalyzed air oxidation of tetrathionate

is very slow under acidic conditions (31). This discrepancy can be explained with the help of Figure 19 which illustrates the reaction profile for a batch experiment conducted at 50°C with the Converter White Metal catalyst over a 23 hour period. Initially (ie. first 240 minutes or 4 hours of reaction), the profile in Figure 19 is similar to the one in Figure 18 c. However, after about 6 hours of reaction the decrease in $S_4O_6^=$ concentration seems to become zero order in nature. The zero order rate expression for the catalyzed oxidation of tetrathionate can be written as shown in (4.8).

$$-\frac{d\,[S_4O_6^=]}{dt} = k_3'\,[S_4O_6^=]^0 \qquad (4.8)$$

The slope of the linear portion of the tetrathionate concentration versus time curve in Figure 19 corresponds to the zero order rate constant k_3' which was found to be 1.034×10^{-6} mol/(L.min) at 50°C. This value is smaller than both $k_1[S_2O_3^=]_o$ (ie. 2.45×10^{-5} mol/(L.min) at 50°C) and $k_2[S_2O_3^=]_o$ (ie. 1.11×10^{-5} mol/(L.min) at 50°C) agreeing with the observed results. A possible explanation as to why the decrease in tetrathionate concentration becomes zero order after 4 to 6 hours of reaction is that, initially, one is observing <u>not</u> the rate of oxidation of tetrathionate but rather its rate of absorption onto the catalyst surface (also explaining the poor sulfur mass balance initially). After 4 to 6 hours, the decrease is due to the limited number of available catalytic sites on the catalyst surface and to the slow oxidation of the $S_4O_6^=$ present on the catalyst surface. This explanation is also supported by the rather small activation

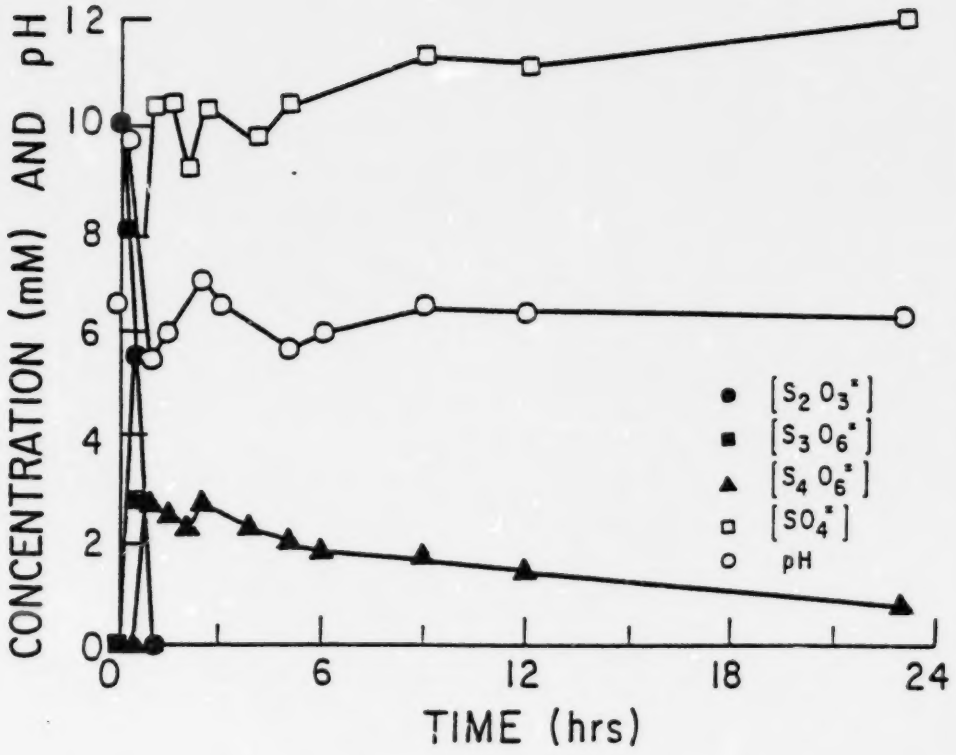


Figure 19. Product distribution profile with Converter White Metal over 23 hour period. Conditions: T = 50°C; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 1.00 g (10.0 mM $S_2O_3^=$); Converter White Metal = 20 g (5 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

energy for the k_3 reaction (ie. 36.1 kJ/mol as shown in Table 8) which is indicative of mixed control (ie. chemical and mass transfer control are of equal importance).

The small rate constant associated with the zero-order nature of the tetrathionate curve explains the very slow degradation of tetrathionate to sulfate observed in the Continuous Reactor Studies section.

The activation energies associated with the k_1 and k_2 steps signify that these two oxidative pathways are chemically controlled whereas the rather small value for the activation energies associated with the k_3 and k_5 steps are indicative of mixed control.

4.1.2 Comparison Between Converter White Metal and Reverbatory Matte

In the Gas Uptake discussion (section 3.2.7), it was found that the Converter White Metal was better at oxidizing thiosulfate than the Reverbatory Matte (ie. initial rate of O_2 consumption for the Converter White Metal was 1.8 times greater than that for the Reverbatory Matte under the same conditions).

Batch experiments are useful in quantifying the differences between the two catalyst materials since one can compare their product distribution patterns under the same conditions.

Figures 20 a and 20 b show the reaction profiles for the Reverbatory Matte and Converter White Metal, respectively, under an otherwise common set of conditions. The results shown in Figures 20 a and 20 b are noteworthy in the following respects:

a) For both the Reverbatory Matte and Converter White Metal

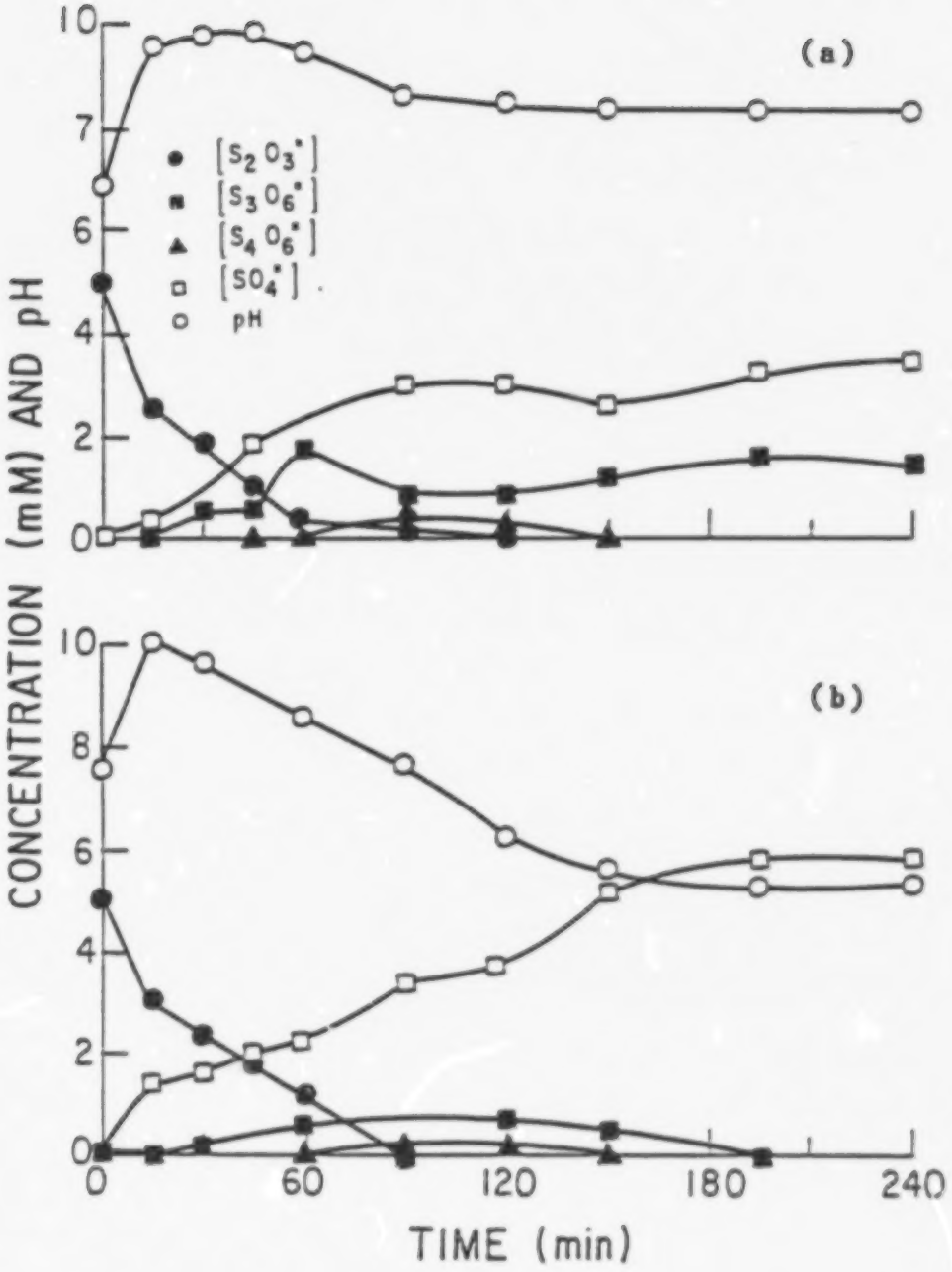


Figure 20. Comparison between Reverbatory Matte and Converter White Metal: (a) Reverbatory Matte; (b) Converter White Metal. Conditions: T = 40 °C; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0 mM $S_2O_3^=$); Converter White Metal = 32 g (8 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

systems, the rate of decrease in $S_2O_3^=$ concentration is approximately the same.

b) The Reverbatory Matte system results in substantial amounts of trithionate which are not easily oxidized. The Converter White Metal system, however, easily oxidizes all the $S_3O_6^=$ present.

c) Both systems produce small amounts of tetrathionate which are slowly oxidized to sulfate.

d) The pH remains above 8 with the Reverbatory Matte system possibly accounting for why the $S_3O_6^=$ does not oxidize easily (see Reaction Chemistry and Kinetics section).

e) After 240 minutes, the sulfate concentration is 3.5 mM and 5.8 mM for the Reverbatory Matte and Converter White Metal systems, respectively.

Since the objective of the present work is to design and develop a catalytic system for the complete oxidation of all thiosalts, the Converter White Metal seems to be the catalyst of choice. Thus, the Converter White Metal was chosen exclusively for all subsequent experiments.

4.1.3 Effect of pH on Thiosulfate Oxidation Chemistry

In all the batch experiments described previously, the pH was allowed to fluctuate freely throughout the experiment. The investigations presented in this section were carried out using a pH controller which added 1M H_2SO_4 to lower the pH to its setpoint of 5.5.

A pH set point value of 5.5 was chosen since Figures 17 and 18 (Reaction Chemistry and Kinetics section) as well as previous

results indicated that a pH in the range of 5 to 6 is the equilibrium pH for the system (ie. the pH naturally remains between 5 and 6 after approximately 150 minutes of reaction for reasons which will be discussed shortly).

A representative product distribution profile for the Converter White Metal system at 40°C is shown in Figure 21. It is of interest to note that the pH controller added acid only during the first 5 to 10 minutes of this experiment to bring the pH of the thiosulfate/catalyst slurry to its desired setpoint of 5.5.

A comparison of the results presented in Figure 21 with those in Figure 18 where the pH was not controlled gives rise to the following interesting points:

a) The decrease in thiosulfate concentration is much quicker when the pH is initially set to 5.5. All $S_2O_3^=$ has been completely oxidized after 60 minutes.

b) Only trace amounts of $S_3O_6^=$ are evident throughout the experiment when the pH is set to 5.5. As discussed in the Reaction Chemistry and Kinetics section, this is probably because trithionate is unstable under neutral or acidic conditions and decomposes quickly to give $S_2O_3^=$, $SO_4^=$ and acid.

c) Conversely, some tetrathionate is formed during the oxidation of $S_2O_3^=$ in accordance with reaction (4.1). Under acidic conditions, $S_4O_6^=$ is stable and is not easily oxidized by the catalyst as shown by the very slow decrease in $S_4O_6^=$ concentration in Figure 21.

d) When the pH is set to 5.5. sulfate is formed relatively

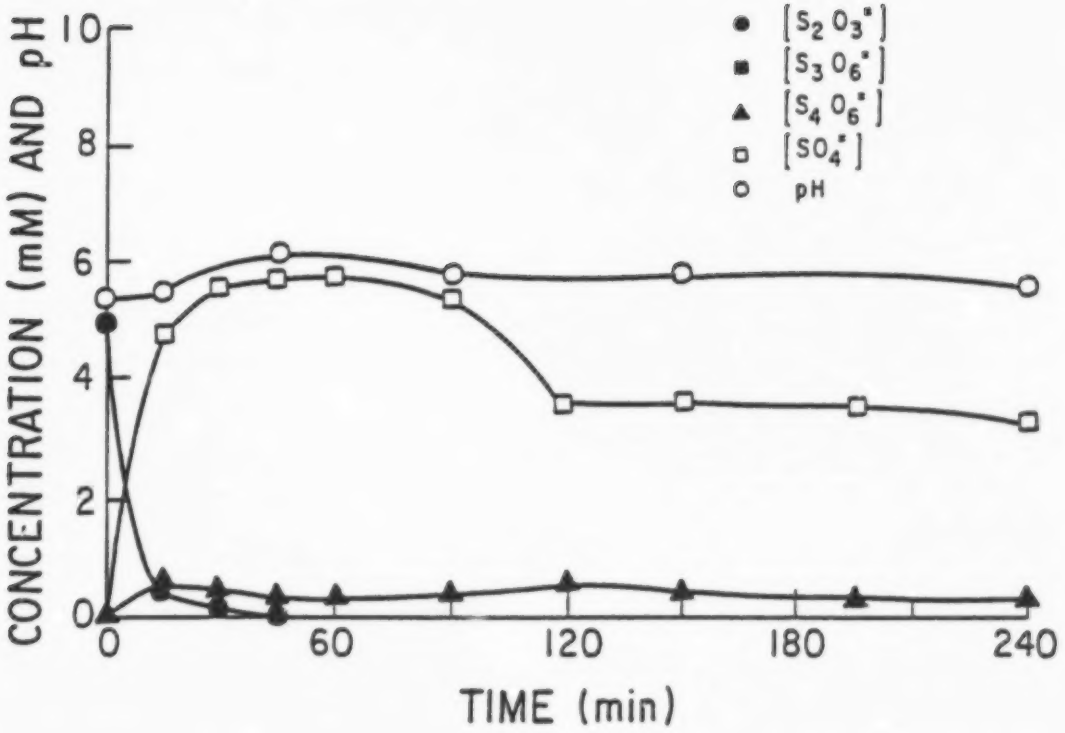


Figure 21. Effect of setpoint pH of 5.5 on thiosalt oxidation rates. Conditions: T = 40°C; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0 mM $S_2O_3^=$); Converter WhiteMetal=16 g (4 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

quickly initially because of reaction (4.2). After reaching a maximum concentration of 5.8 mM, the sulfate concentration decreases to a value of 3.3 mM after 240 minutes because the sulfate produced reacts with the copper present in solution to give basic copper sulfate precipitates.

The formation of the basic copper sulfate precipitate mentioned above deserves some further discussion. As thiosulfate and other thiospecies are oxidized, acid is produced as shown in reactions (4.2), (4.4) and (4.6). This acid reduces the pH of the reaction medium as shown by the results provided in Figures 17 and 18. Also, for the results shown in Figure 21, the use of the pH controller resulted in some addition of 1M H_2SO_4 during the first 5 - 10 minutes of the experiment to bring the initial pH down to 5.5. All of these forms of acid have the potential to leach metallic copper or Cu(I) from the sulfide ore concentrate to form Cu^{2+} (the leaching process is described in section 3.2.8). As discussed in Appendix II, the major acid consumer appears to be Cu_2O, followed by Cu and Cu_2S. Thus, the reduced state of copper in the sulfide acts as a potential sink for the acid which is produced in reactions (4.2), (4.4) and (4.6), as well as for the acid added to lower the pH of the reaction media to its prescribed setpoint.

The resulting Cu^{2+} ions can then react with sulfate present in solution to form copper sulfate (equation (4.9)) which can then precipitate to produce a basic copper sulfate precipitate, such as brochantite, as shown in equation (4.10).

$$Cu^{2+} + SO_4^{=} \longrightarrow CuSO_4 \qquad (4.9)$$

$$4\ CuSO_4 + 6\ H_2O \longrightarrow 3\ Cu(OH)_2.CuSO_4 + 3\ H_2SO_4 \qquad (4.10)$$

The formation of these precipitates can be qualitatively explained by means of a potential - pH diagram which describes in a graphical manner the equilibrium between aqueous solution and solid phase plotted as the single electrode potential versus pH.

Figure 22 shows a Eh - pH diagram for the system $CuSO_4$-H_2SO_4-H_2O at 100°C (23). For positive potentials and acidic conditions, both antherite (2 $Cu(OH)_2.CuSO_4$) and brochantite (3 $Cu(OH)_2.CuSO_4$) are formed. Antherite precipitates when the pH lies between 3.3 and 5.1; brochantite precipitates when the pH falls between 5.1 and 5.6. The formation of these insoluble precipitates helps to account for the rather poor sulfur mass balances experienced in both the gas uptake and batch experiments.

In conclusion, the equilibrium pH remains between 5 and 6 since under those conditions the aqueous solution is in equilibrium with the solid phase (ie. brochantite and/or antherite). This catalyst system appears to behave as a natural buffer explaining why the pH does not fall below 5 during the entire course of the thiosulfate oxidation experiment. This effect will also be discussed later in the Continuous Reactor Studies section.

4.1.4 Reuse of Catalyst in Batch Type Studies

After being used once in a batch experiment, the used Converter White Metal catalyst was washed several times with distilled water, suction filtered and allowed to dry in air. It

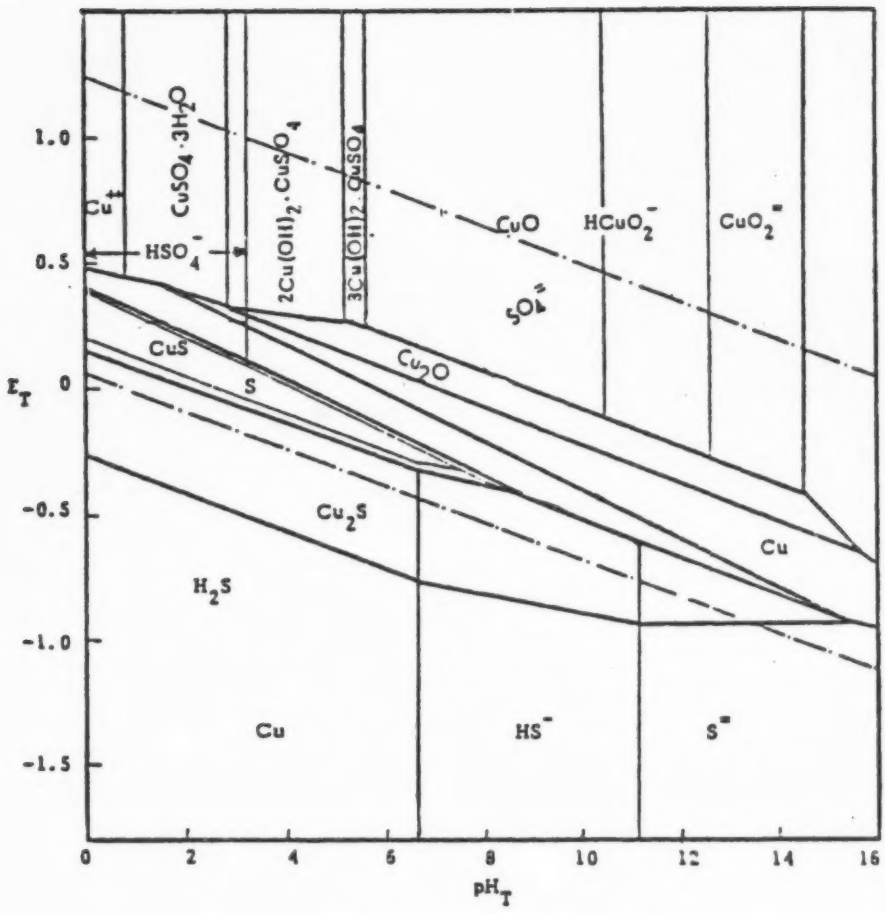


Figure 22. Potential - pH Diagram for the System $CuSO_4$-H_2SO_4-H_2O at 100°C. (All Species are at Unit Activity). (23)

was then subsequently used in another analogous batch experiment. The results indicate no loss in activity relative to the initial experiment over an 8 hour period.

The long term behaviour of the ore concentrates will be discussed in greater detail in the Continuous Reactor Studies section.

4.1.5 Effect of Catalyst Loading on Thioanion Oxidation Rates

Figure 23 shows two product distribution patterns obtained with the Converter White Metal catalyst system at two different catalyst loadings: 4 (w/v) % and 8 (w/v) %. One would expect that an increase in the catalyst loading will increase the rates of oxidation since the rate constants are pseudo-first order in nature and comprise the catalyst concentration in the slurry.

A comparison of the two reaction patterns shown in Figure 23 results in the following deductions:

a) Increasing the catalyst loading greatly enhances the rate of oxidation of thiosulfate.

b) In both cases, the pH decreases from approximately 10 to 5 over the course of the experiment due to the production of acid in the oxidation process (reactions (4.2), (4.4), (4.5) and (4.6)).

c) With an 8 (w/v) % loading, less trithionate and tetrathionate are produced. These are oxidized more rapidly to sulfate during the initial stages of the reaction.

d) The mass balance is poorer with the 8 (w/v) % loading due to its greater adsorption capacity for thioanions relative to a 4

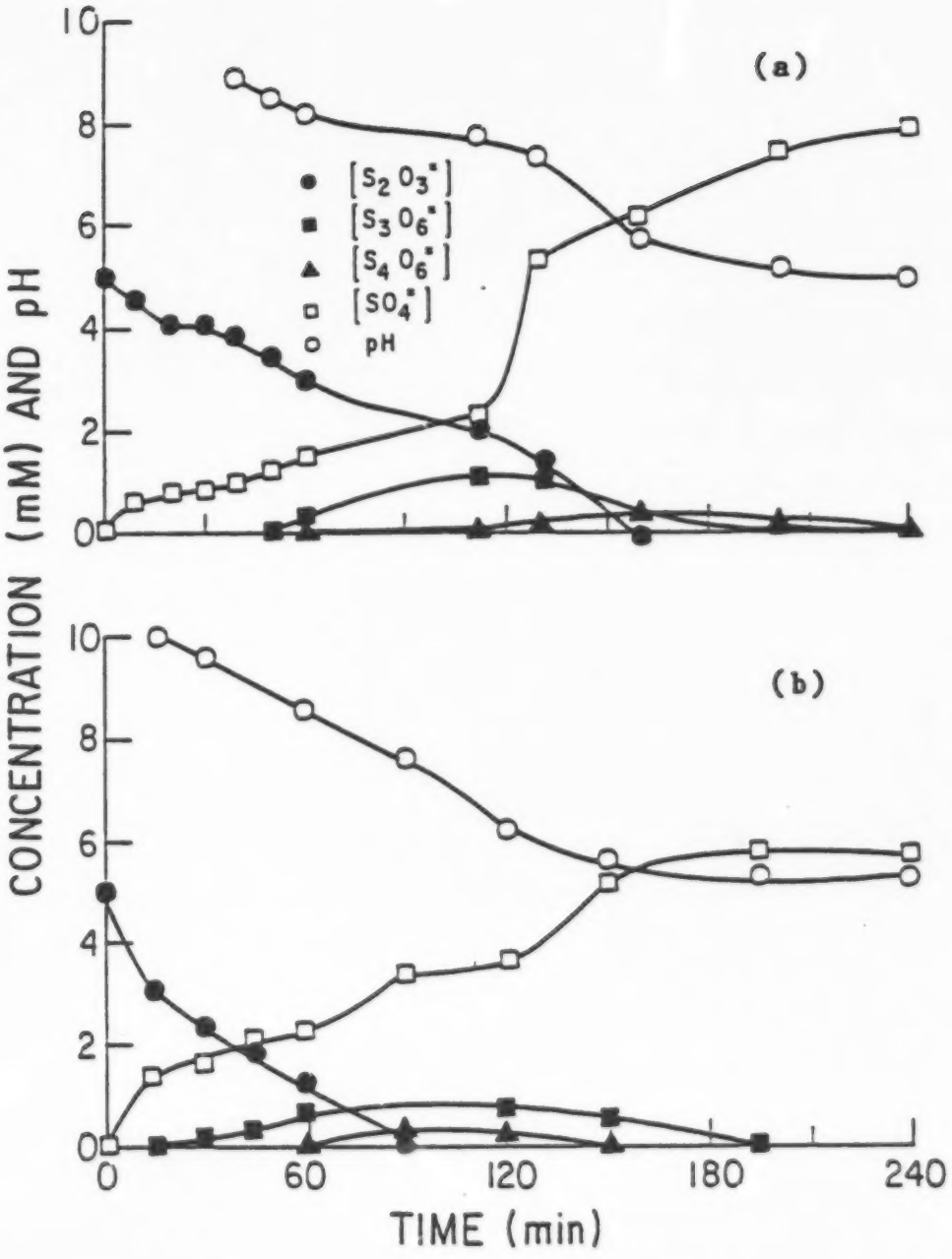


Figure 23. Effect of catalyst loading on thiosalt oxidation rates: (a) 4 (w/v) % catalyst loading, (b) 8 (w/v) % catalyst loading. Conditions: $T = 40^{\circ}C$; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0 mM $S_2O_3^=$); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

(w/v) % loading and to the increased formation of basic copper sulfate precipitates.

Hence, increasing the catalyst loading will augment the rate of oxidation and/or removal of all thiosalts. It is therefore advantageous to use the highest catalyst loading possible with the batch reactor.

4.1.6 Effect of Temperature on Thioanion Oxidation Rates

Batch experiments with the Converter White Metal system were performed over the temperature range of 30°C to 60°C at a 4 (w/v) % catalyst loading. The results of these studies have been shown previously in Figures 18 a to 18 d. The following observations are worth mentionning:

a) 30°C: At this temperature, the $S_2O_3^=$ is not completely oxidized to $SO_4^=$. Considerable amounts of $S_3O_6^=$ (ie. 3mM) are produced but are not completely destroyed over a 240 minute period. A very small amount of sulfate is produced; no tetrathionate is evident. The pH remains above 8 throughout the experiment.

b) 40°C: The thiosulfate is slowly oxidized and has completely disappeared after 160 minutes. Some trithionate is produced but it is quickly destroyed thereby producing sulfate and acid (reactions (4.5) and/or (4.6)). This explains the quick increase in sulfate concentration and decrease in pH between 120 and 180 minutes. Some tetrathionate still remains after 240 minutes of reaction.

c) 50°C: The shape of the $S_2O_3^=$ curve is erratic due to the

rapid decomposition of tetrathionate and trithionate to form thiosulfate (reactions (4.3) and (4.5), respectively). The pH quickly decreases to 5 as the thiosalts are oxidized. After 240 minutes the sulfate concentration is 7 mM.

d) 60°C: At this elevated temperature, the decrease in thiosulfate is very rapid. Considerable amounts (ie. 3 mM) of trithionate are produced; however, they are completely destroyed after 150 minutes of reaction. As the pH decreases, tetrathionate appears before being slowly oxidized. After 240 minutes, the $SO_4^=$ concentration is 6 mM.

Therefore, as expected, high temperatures yield the most rapid oxidation rates. However, the rather small activation energies reported in the Kinetics section indicate that the rates are not very temperature sensitive over the range of conditions investigated.

4.2 Use of Synthetic Effluent with 30 (w/v) % Catalyst Loading at 30°C

In order to gain information which could prove useful for the assessment of the practical feasibility of the Converter White Metal catalyst system, some work was carried out using low temperatures (ie. 30°C) but with increased catalyst loadings.

As discussed in section 4.1.6 (Effect of Temperature), the rate of oxidation of all thiosalts diminishes as the temperature is lowered. However, the activation energies are relatively low (section 4.1.1) indicating that the rates have a rather low temperature dependency.

To offset the decrease in rate due to lowering the

temperature to 30°C, the use of high catalyst loadings was examined. It was shown in the Effect of Catalyst Loading (section 4.1.5) that increasing the catalyst loading significantly augments the oxidation rates.

4.2.1 Preliminary Investigations

A representative product distribution profile for the Converter White Metal system (30 (w/v) % catalyst loading at 30° C) is shown in Figure 24.

The pH remained above 8 throughout this oxidation experiment. Very little $S_4O_6^=$ is produced initially since it is not stable under basic conditions and decomposes quickly to give $S_2O_3^=$ and $S_3O_6^=$ (reaction (4.3)). This probably accounts for the strange shape of the trithionate and thiosulfate curves. After 300 minutes, some $S_3O_6^=$ still remains since it only decomposes readily under neutral or acidic conditions to give $S_2O_3^=$ and $SO_4^=$ (reaction (4.5)).

The sulfur mass balance is poor after 300 minutes (ie. about 60 % of total sulfur accounted for) due to the formation of basic copper sulfate precipitates and to the increased thioanion adsorption capacity of the catalyst system with the higher catalyst loadings.

A comparison of Figure 24 with Figure 18 (section 4.1.6) results in three further interesting observations:

a) The rates of oxidation of all thiosalts at 30°C is much more rapid with a 30 (w/v) % loading than with a 4 (w/v) % loading. Thus, the pseudo-first order rate constants presented in the Reaction Chemistry and Kinetics section (section 4.1.1) do

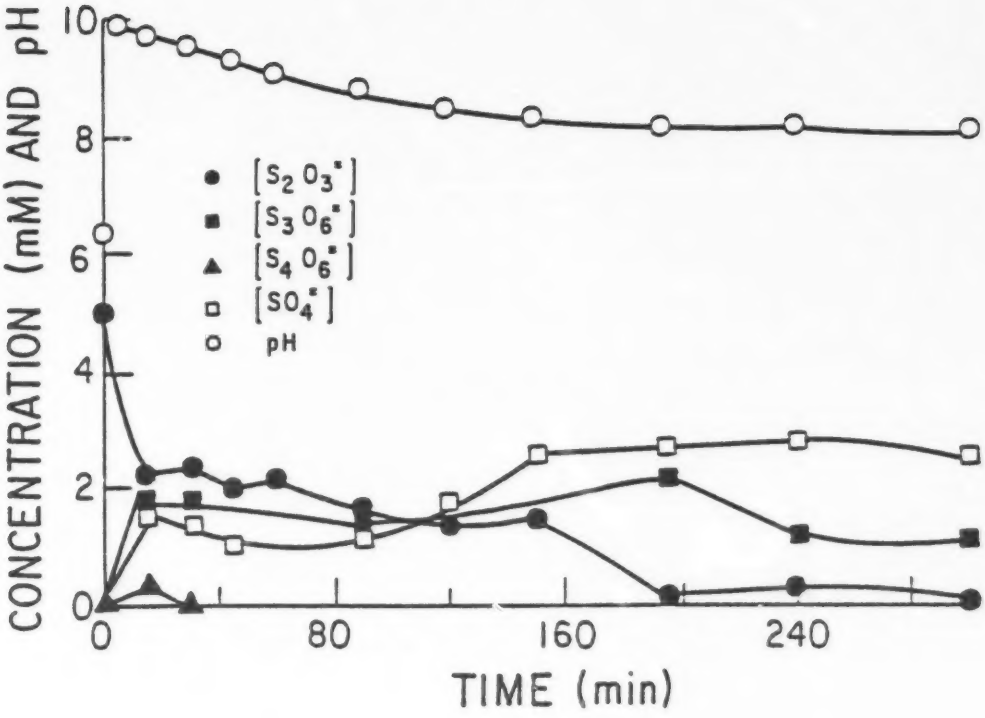


Figure 24. Representative product distribution profile for Converter White Metal. Conditions: T = 30°C; 400 mL distilled water; $Na_2S_2O_3.5H_2O$ = 0.500 g (5.0 mM $S_2O_3^=$); Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm; pH not set.

exhibit a dependance on the catalyst concentration, as expected.

b) At 30°C and 30 (w/v) % loading, the decrease in $S_2O_3^=$ is similar to that obtained at 50°C and 4 (w/v) %; the production and destruction of $S_3O_6^=$ resembles that at 40°C and 4 (w/v) %; the minimal production of $S_4O_6^=$ is advantageous.

c) The sulfur mass balances at higher loadings are generally poorer (ie. less than 60 to 70 % of total S accounted for at a 30 (w/v) % loading; whereas, over 80 % of total S is accounted for at a 4 (w/v) % loading) since more copper is leached into solution at higher loadings thereby increasing the formation of basic copper sulfate precipitates. Furthermore, higher amounts of thioanion adsorption will undoubtedly occur with the higher catalyst loadings.

Since these preliminary investigations indicated that lower temperatures and high loadings could yield reasonable oxidation rates, further experiments under these conditions were carried out with a synthetic effluent having a thioanion composition more typical of that to be encountered at a mill site. The synthetic effluent previously used consisted only of thiosulfate. In order to approximate the composition of real mill effluent, various synthetic effluents of varying composition were prepared.

Figure 25 shows typical product distribution profiles for a synthetic effluent ($[S_2O_3^=]$ = 14.28 mM, $[S_4O_6^=]$ = 0.89 mM, $[SO_4^=]$ = 0.90 mM, $[Fe^{2+}]$ = 50 ppm) with the pH allowed to fluctuate freely as well as when the pH was set to 5.5.

In Figure 25 a, the pH remained above 9 throughout the experiment. After 240 minutes of reaction, considerable amounts of $S_2O_3^=$ and $S_3O_6^=$ were present but the initially present $S_4O_6^=$

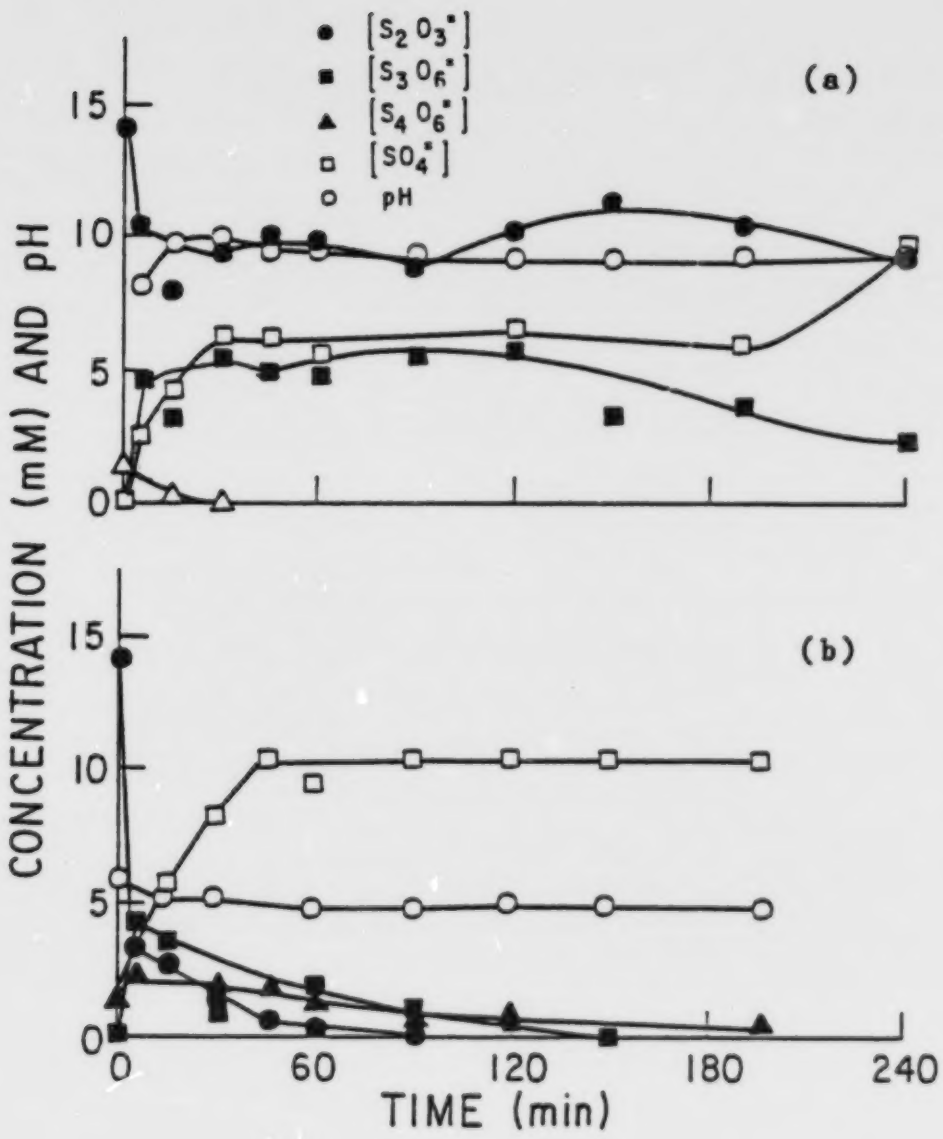


Figure 25. Effect of pH on the thioanion oxidation rates for the Converter White Metal system with synthetic effluent of the following initial composition: $[S_2O_3^{=}]$ = 14.28 mM; $[S_4O_6^{=}]$ = 0.89 mM; $[SO_4^{=}]$ = 0.90 mM; $[Fe^{2+}]$ = 50 ppm.
(a) pH allowed to fluctuate freely, (b) pH set to 5.5. Conditions: T = 30°C; 400 mL synthetic effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm.

was quickly oxidized. At this reaction time, the $SO_4^=$ concentration was 9.0 mM. Fe^{2+} is known to catalyze the oxidation of $S_2O_3^=$ to $S_3O_6^=$ (2); therefore, the presence of 50 ppm Fe^{2+} in the synthetic effluent may account for the considerable formation of trithionate.

When the pH controller was used to add 1M H_2SO_4 to lower the pH to its set point of 5.5, $S_2O_3^=$, $S_3O_6^=$ and $S_4O_6^=$ were rapidly oxidized to $SO_4^=$ as seen from the results presented in Figure 25 b. After 195 minutes of reaction, the $SO_4^=$ concentration was 10.4 mM.

As found previously, the pH of the reaction medium has a pronounced effect on the thioanion oxidation rates, a slightly acidic pH of 5.5 being preferable.

4.2.2 Effect of the Presence of Ca^{2+} on Thioanion Oxidation Rates

Since real thiosalt effluent is saturated with calcium sulfate, it was felt that the sulfate produced during the catalytic oxidation process might precipitate as $CaSO_4$ thereby coating the catalyst particles and lowering their subsequent catalytic activity towards the thioanion oxidation process.

In order to study this effect, a synthetic effluent of the following composition was prepared: $[S_2O_3^=]$ = 7.40 mM, $[S_3O_6^=]$ = 1.28 mM, $[S_4O_6^=]$ = 1.05 mM, $[SO_4^=]$ = 10.9 mM, $[Fe^{2+}]$ = 65.1 ppm, and $[Ca^{2+}]$ = 428 ppm.

The product distribution profiles shown in Figure 26 for the fresh catalyst and its reuse are nearly identical. In both cases the $S_2O_3^=$ has been completely oxidized after 240 minutes and only

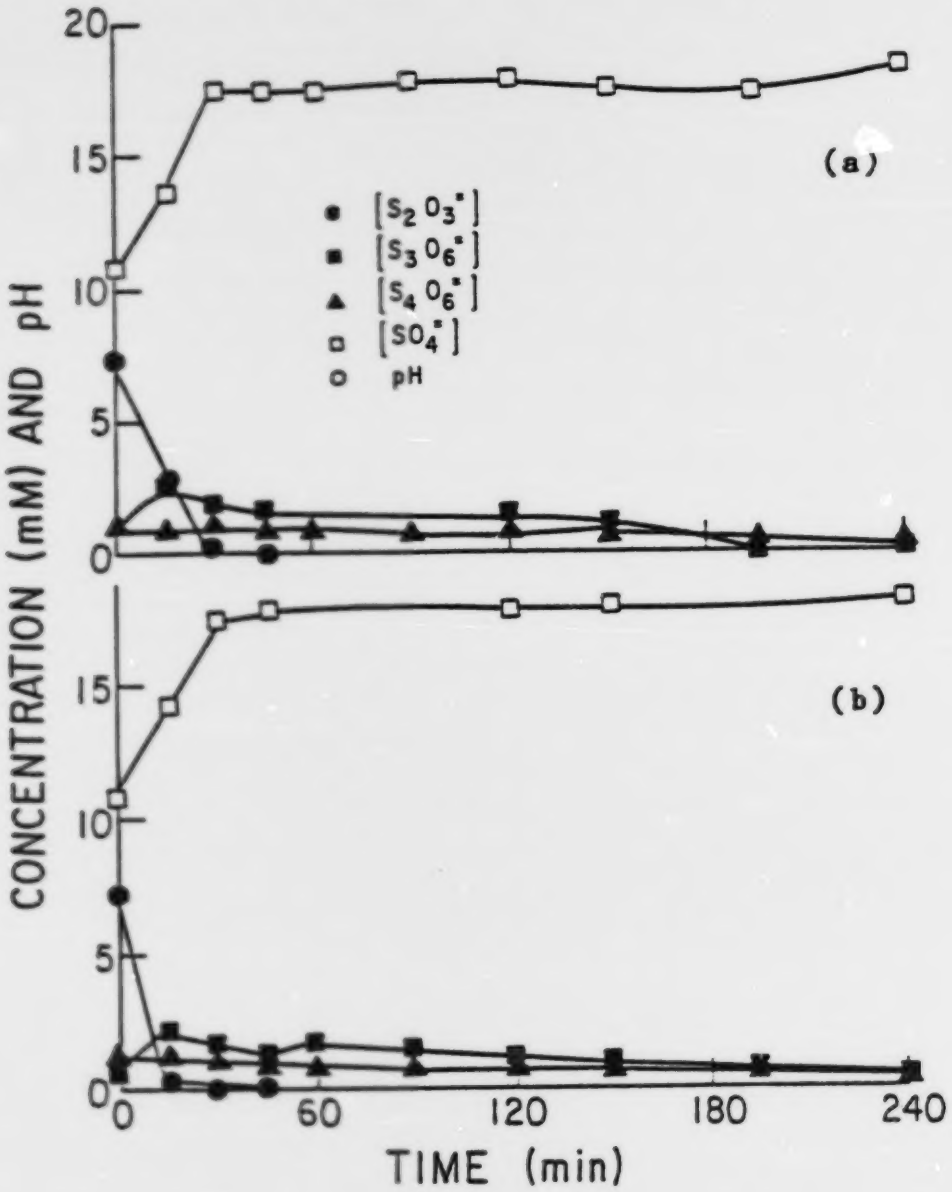


Figure 26. Effect of the presence of Ca^{2+} on the thioanion oxidation rates for the Converter White Metal system with synthetic effluent of the following initial composition: $[S_2O_3^=]$ = 7.40 mM; $[S_3O_6^=]$ = 1.28 mM; $[S_4O_6^=]$ = 1.05 mM; $[SO_4^=]$ = 10.9 mM; $[Fe^{2+}]$ = 65.1 ppm; $[Ca^{2+}]$ = 428 ppm. (a) fresh catalyst, (b) reused catalyst. Conditions: T = 30°C; 400 mL synthetic effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring = 700 rpm; setpoint pH = 5.5.

trace amounts of $S_4O_6^=$ remain for the fresh catalyst; however, the used catalyst still had measurable quantities of $S_3O_6^=$ and $S_4O_6^=$ after 240 minutes of reaction. The $SO_4^=$ concentration remains constant after 45 minutes since the synthetic solution is now completely saturated with calcium sulfate.

Thus, over a period of up to 8 hours, the $CaSO_4$ does not appear to significantly hinder the catalyst's effectiveness for catalyzing thioanion oxidation.

4.3 Use of Real Effluent with 30 (w/v) % Catalyst Loading at 30°C

Various real mill effluent samples from Brunswick Mining and Smelting were obtained. Real mill effluent, also known as reclaim water, contains both tailings decant and thickener overflow solutions. Generally, these two solutions are blended together in the ratio of 80 % tailings decant to 20 % thickener overflow solutions to produce actual thiosalt effluent. Several batch experiments were conducted with real effluents to study their behaviour under the reaction conditions employed for studies outlined in the synthetic effluent sections (sections 4.1 and 4.2).

It should be noted that the composition of the real effluent changed very slowly with time (even if refrigerated). Generally, the $S_2O_3^=$ and $S_3O_5^=$ concentrations decreased slightly with time whereas the $S_4O_6^=$ and $SO_4^=$ concentrations increased due to the slow interconversion between the various thioanions (2). This explains why the initial thioanion concentration differs somewhat from experiment to experiment.

4.3.1 Comparison Between Synthetic and Real Effluents

The composition of the synthetic effluent (section 4.2) was chosen to resemble that of real effluent supplied by Brunswick Mining and Smelting. The synthetic effluent contained thiosulfate, trithionate, tetrathionate, sulfate, ferrous ions and calcium ions all of which are present in real effluent.

Product distribution profiles for the catalytic oxidation of synthetic and real effluents in the presence of Converter White Metal are shown in Figures 27 a and 27 b, respectively.

Other than the fact that the real effluent has higher initial polythionate concentrations, both profiles are similar indicating that the real effluent behaves essentially the same as synthetic effluent to oxidative treatment by the catalytic Converter White Metal system.

4.3.2 Reproducibility of Results

To determine if the batch product distribution profiles obtained with real effluent were reproducible, two batch experiments were performed under the same conditions with the Converter White Metal catalyst system.

The results for these two experiments are shown in Figure 28. It should be noted that the composition of the real effluent changed slightly in the interval between these two experiments due to the slow interconversion between the various thioanion species. Both reaction profiles are essentially the same indicating that the results obtained with real effluent are indeed reproducible.

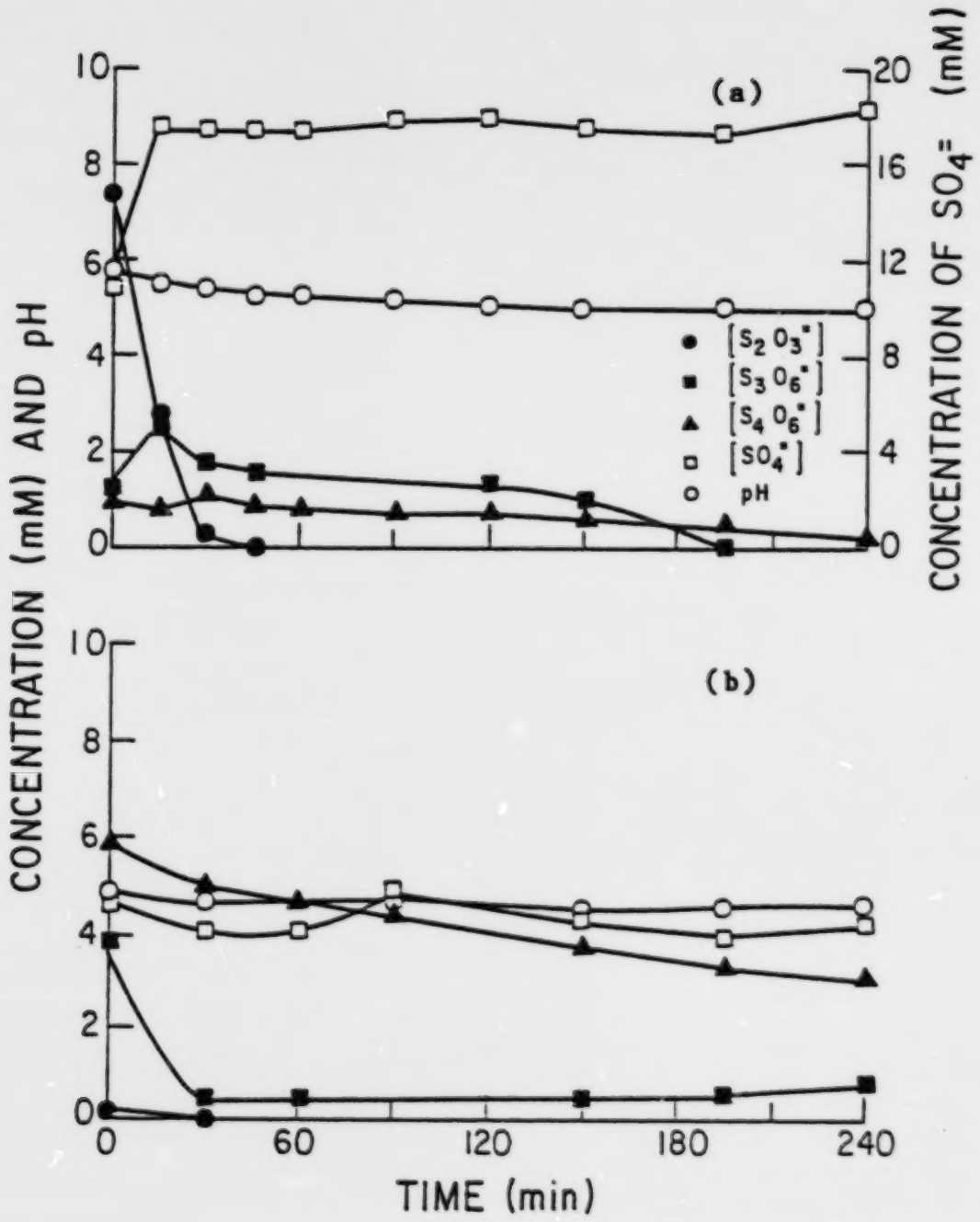


Figure 27. Comparison between synthetic and real mill effluent. (a) synthetic effluent, (b) real effluent. Conditions: T = 30°C; 400 mL effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring speed = 700 rpm; setpoint pH = 5.5.

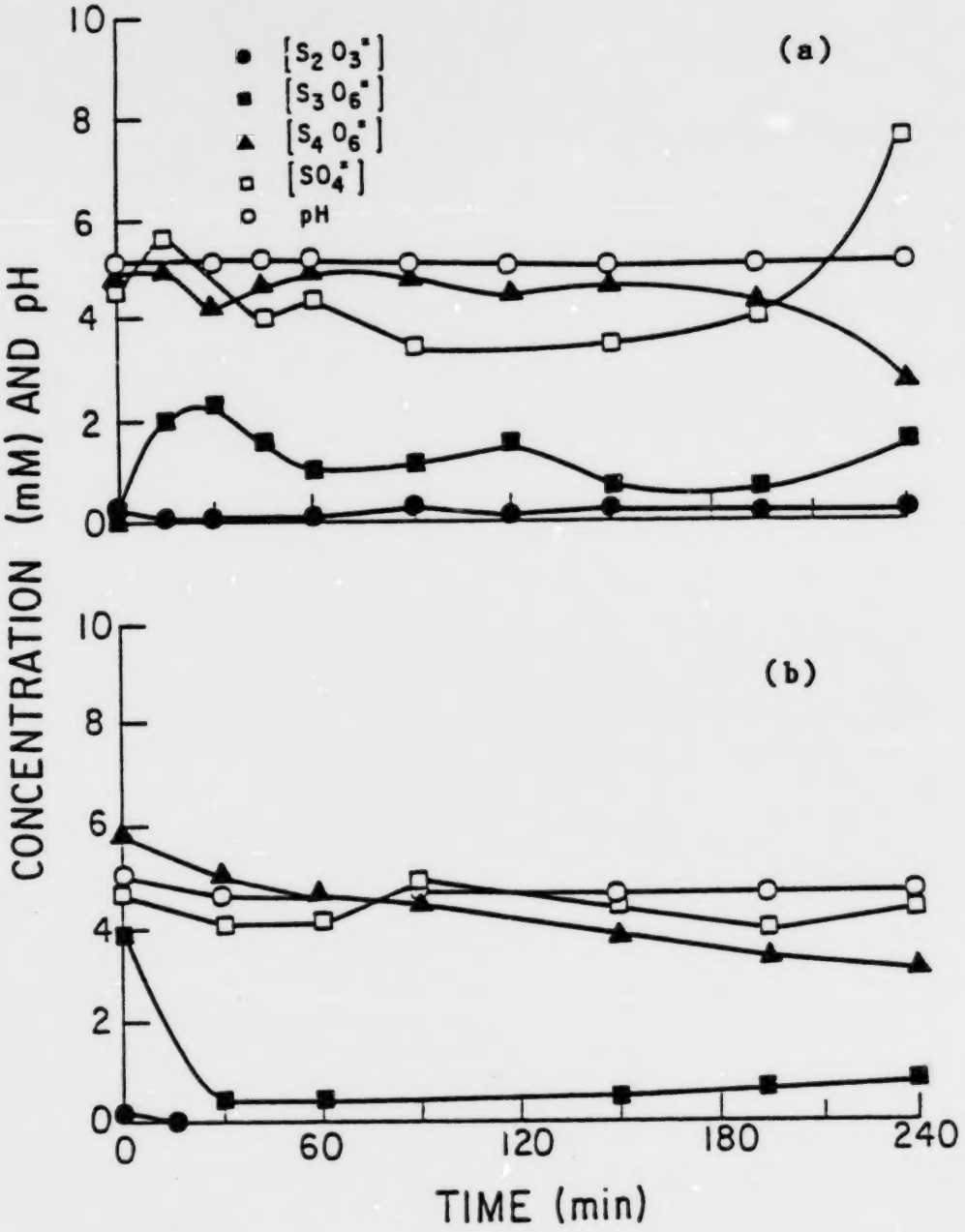


Figure 28. Reproducibility of product distribution profiles for the Converter White Metal system with real mill effluent. (a) experiment number 1, (b) experiment number 2. Conditions: T = 30°C; 400 mL real mill effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring = 700 rpm; setpoint pH = 5.5.

4.3.3 Effect of pH on Thioanion Oxidation Rates

In sections 4.1.3 and 4.2.1, it was found with synthetic effluent that a slightly acidic pH of about 5 to 6 yielded the best thiosalt oxidation rates. Experiments at set pH values of 5.5 and 4.0 were done with the real effluent containing both the tailings decant and the thickener overflow solutions.

The results shown in Figure 29 lead us to conclude the following:

a) All $S_2O_3^=$ was quickly oxidized at both pH values.

b) The decrease in trithionate concentration is quite rapid initially. This is because, under acidic conditions, trithionate decomposes to give $S_2O_3^=$ (which is quickly oxidized) as well as $SO_4^=$ and acid (reaction (4.5)).

c) The decrease in tetrathionate is more rapid at the lower pH values.

d) In both cases the sulfate concentration remains constant throughout the experiment. As previously explained, this is because the solution is saturated with $SO_4^=$. Any sulfate which is produced is precipatated as $CaSO_4$ or as basic $CuSO_4$. The solubility of these compounds is higher at lower pH values (26).

e) Decreasing the pH to 4.0 greatly increases the amount of soluble copper in solution.

Although the rate of oxidation of the thiospecies is higher at a pH of 4.0 (Figure 29 b), the amount of copper leached from the catalyst is much greater. A pH of 5.5 was selected for further experiments since it represented a good compromise between rapid thiosalt oxidation rates and a relatively low

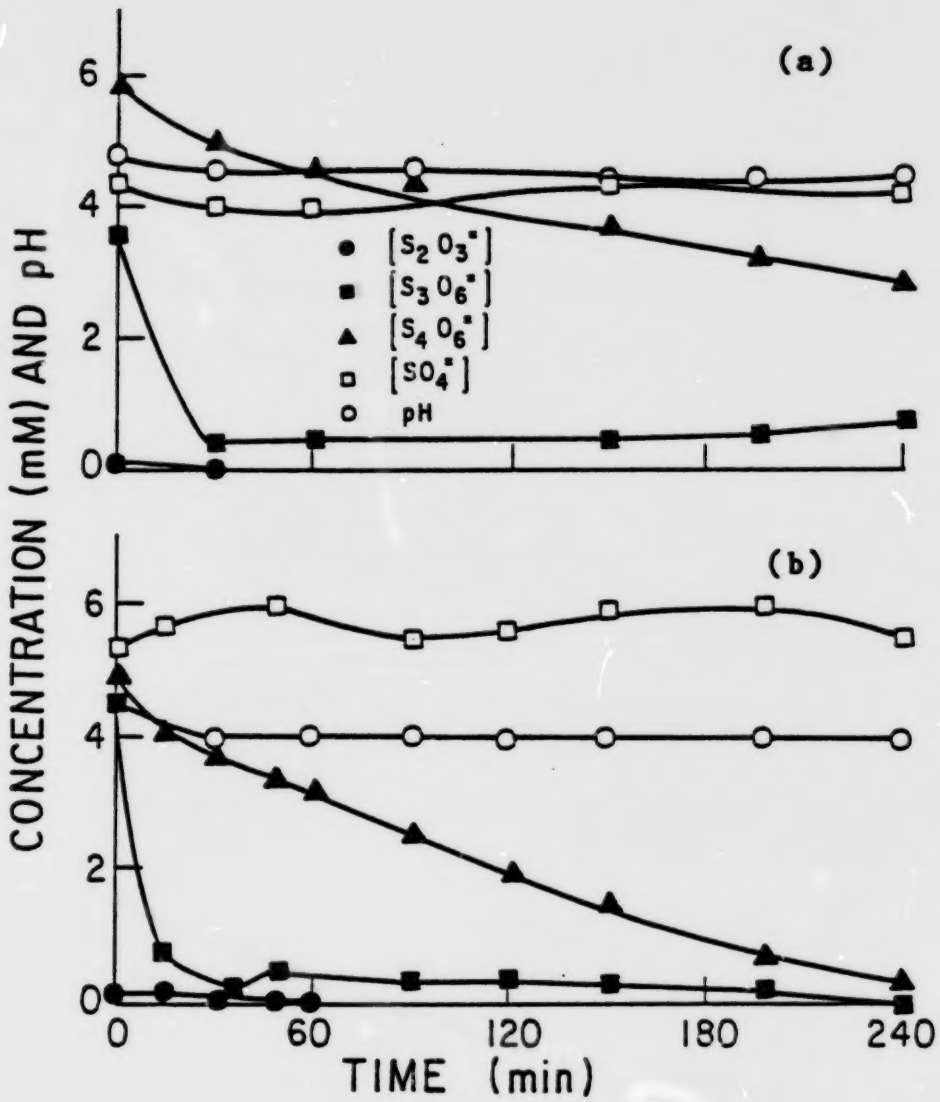


Figure 29. Effect of setpoint pH on the thioanion oxidation rates for the Converter White Metal system with real mill effluent. (a) setpoint pH of 5.5, (b) setpoint pH of 4.0. Conditions: T = 30°C; 400 mL real mill effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring = 700 rpm.

degree of copper leaching from the catalyst material.

4.3.4 Use of Tailings Decant Solution from Brunswick Mining and Smelting

Originally, separate barrels of tailings decant solution and thickener overflow solution were to be examined for thiosalt oxidation. As previously explained, the solutions were to be blended in the ratio of 80 % tailings decant to 20 % thickener overflow to produce reclaim water. However, because of poor shipping procedures, only the tailings decant water was received and consequently examinations were restricted to this material.

The composition of the tailings decant solution (when first received) was as follows:

Drum	$[S_2O_3^{=}]$ (mM)	$[S_3O_6^{=}]$ (mM)	$[S_4O_6^{=}]$ (mM)	$[SO_4^{=}]$ (mM)	$[Cu^{2+}]$ (ppm)	$[Fe^{2+}]$ (ppm)	$[Ca^{2+}]$ (ppm)	pH
1	5.01	0.62	0.39	22.2	0	99.6	536	6.5
2	3.09	0.58	0.49	17.8	0	61.8	492	6.2

The tailings decant solution appeared to be low in total thiosalt content (presumably the thickener overflow contains much higher thiosalt concentrations) but rather high in iron and calcium levels.

The results for two typical batch experiments, conducted with the two different drums of the decant solution, are shown in Figure 30.

Both profiles are similar. The catalyst easily oxidized all of the thiosalts present. In Figure 30 a, the thiosulfate, trithionate and tetrathionate have been completely destroyed

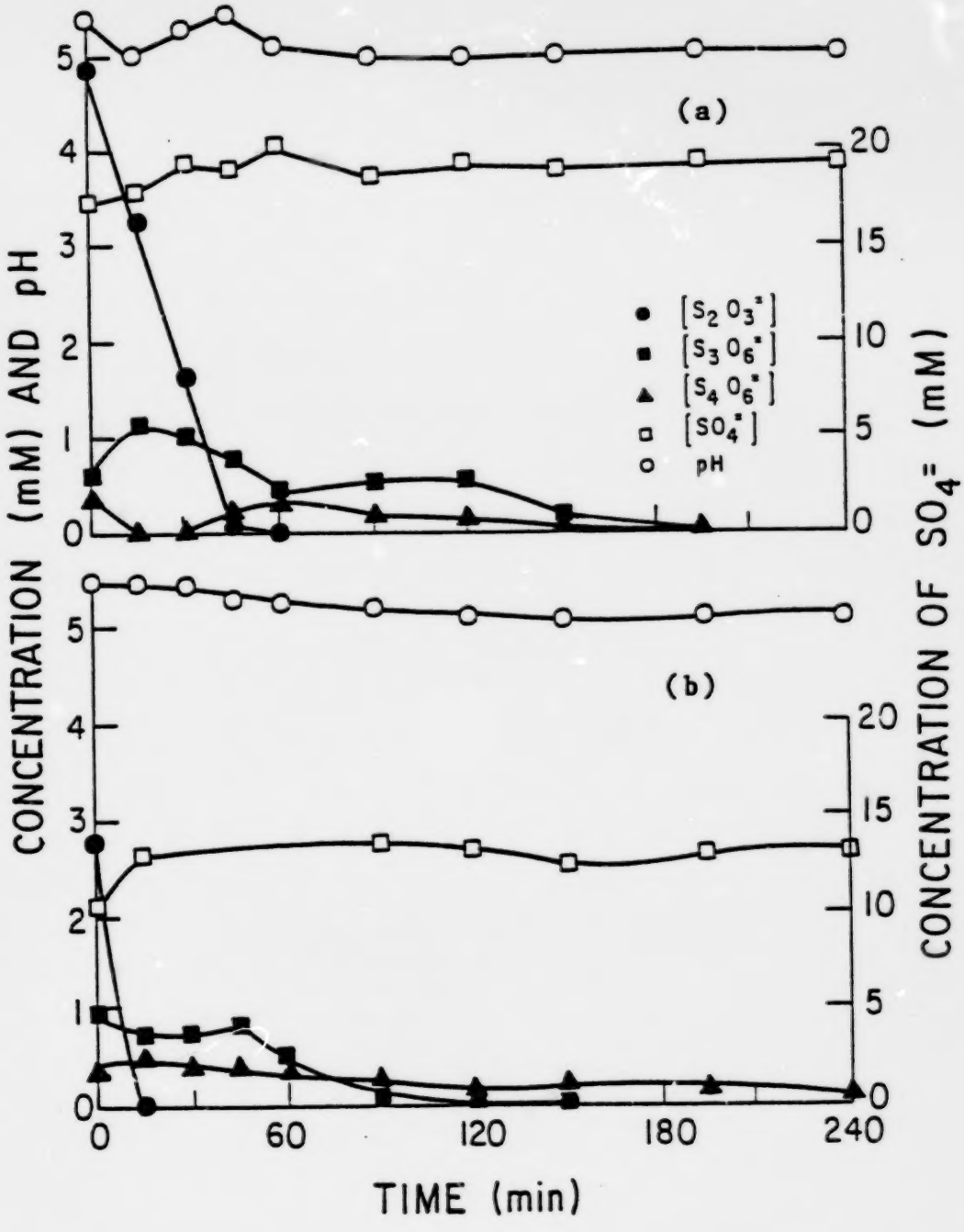


Figure 30. Representative product distribution profiles for the Converter White Metal system with solution from two different drums of tailings decant solution. (a) drum number 1, (b) drum number 2. Conditions: T = 30°C; 400 mL real mill effluent; Converter White Metal = 120 g (30 (w/v) % catalyst loading); air flow > 600 mL/min.; 45 um < d_p < 125 um; stirring = 700 rpm; setpoint pH = 5.5.

after 45, 195, and 195 minutes, respectively. The sulfate concentration appears to remain constant throughout the experiment because the solution is initially saturated with $SO_4^=$.

In Figure 30 b, the thiosulfate and trithionate have been oxidized after 15 and 150 minutes, respectively. However, trace amounts of tetrathionate remain after 240 minutes (ie. 0.090 mM).

Hence, the Converter White Metal can easily oxidize to sulfate the low thiosalt levels present in the tailings decant solution. No further experiments were performed on real effluent since the tailings decant water behaved essentially the same as synthetic effluent.

The batch experiments were usually conducted over a period of 4 hours. Consequently, these relatively short experiments do not offer a reliable insight into the long term behaviour of catalyst used on a continuous basis. Thus, as this survey work on the pertinent features of the catalyst system was progressing, the long term activity of the most promising catalytic materials was studied by conducting a series of continuous reactor studies which are discussed in the following sections.

5. CONTINUOUS REACTOR EXPERIMENTS

While investigations continued on batch and oxygen uptake experiments to define important reaction variables and features, preliminary continuous runs were initiated using a 10 L stainless steel slurry reactor (see Experimental section).

The activity of synthetic copper (I) sulfide (Cu_2S), investigated in previous work (11), was studied initially in order to gain operating experience and to determine important reactor variables and limitations. Since oxygen uptake and batch experiments identified Converter White Metal and Reverbatory Matte as the most promising catalysts, these materials were also examined on a preliminary continuous basis. Subsequently, more detailed runs were carried out using Converter White Metal catalyst. This catalyst was selected on the basis of batch and continuous experiments as having the best overall potential as a thioanion oxidation catalyst in the present study.

5.1 Preliminary Runs

5.1.1 Blank Run

A "blank" run (ie. no catalyst in reactor) was carried out over a six day period to determine if there was any significant thioanion oxidation or interconversion under the same reaction conditions as those employed in the catalytic continuous studies. The thioanion concentrations for the feed and effluent, shown in Table 10, indicate that there is no noticeable change under these conditions.

Table 10. Thioanion, sulfate, total sulfur concentrations and pH for blank 6 day run. Run conditions: temp = 50°C, feed flow = 6.1 mL/min, air flow = 700 mL/min.

Stream	$[S_2O_3^=]$, mM	$[S_3O_6^=]$, mM	$[S_4O_6^=]$, mM	$[SO_4^=]$, mM	[total S], mM	pH
feed	11.3	0	0.41	1.0	25.2	7.4
effluent	11.4	0	0.57	1.3	26.5	8.7

Table 11. Stability test of synthetic thiosulfate feed (50L batch) at ambient temperatures (24 - 25°C). Trithionate concentration negligible.

Day	$[S_2O_3^=]$, mM	$[S_4O_6^=]$, mM	pH
0	10.40	0.49	---
1	10.45	0.45	---
4	10.47	0.48	8.1
6	10.34	0.46	8.3
9	9.97	0.61	8.3
10	10.49	0.44	8.3

The synthetic thiosulfate feed solution used in all preliminary runs exhibited fair stability, as shown in Table 11 for consecutive analysis over a ten day period. Typically, a 50 L batch of feed solution would be consumed within 6 to 7 days.

5.1.2 Copper (I) Sulfide catalyst

The effluent composition and reactor pH over a 26 day continuous run with 5 (w/v) % slurry loading of synthetic Cu_2S catalyst is shown graphically in Figure 31 (compiled data for this run and all subsequent continuous runs presented in this report were tabulated and are presented in Appendix V). A feed of 11.5 mM $Na_2S_2O_3$ and 0.4 mM $Na_2S_4O_6$ (averaged concentrations) was used throughout the run.

Approximate operating parameters for the Cu_2S continuous experiment were estimated from previous work (11). With initial conditions of 50°C, 7.0 mL/min feed flow and 700 mL/min air flow (days 1 - 4), the feed $S_2O_3^=$ was converted mostly to $SO_4^=$ (16 - 18 mM) and some $S_4O_6^=$ (0.8 - 1 mM). The 700 mL/min air rate provided about 40 times the theoretical amount of oxygen (see equations (3.1) and 3.6)) needed to completely oxidize the feed thioanions to sulfate.

When the temperature or air rate was lowered (days 15 - 23) or the feed rate raised (days 6 - 10), the $SO_4^=$ level decreased and there was a corresponding increase in $S_4O_6^=$. This is consistent with previous batch data using Cu_2S (11) and similar to batch results obtained with Converter White Metal in this study (see section 4.1.1) in that there is rapid oxidation of $S_2O_3^=$ to $SO_4^=$ and some $S_4O_6^=$, followed by slow oxidation of $S_4O_6^=$

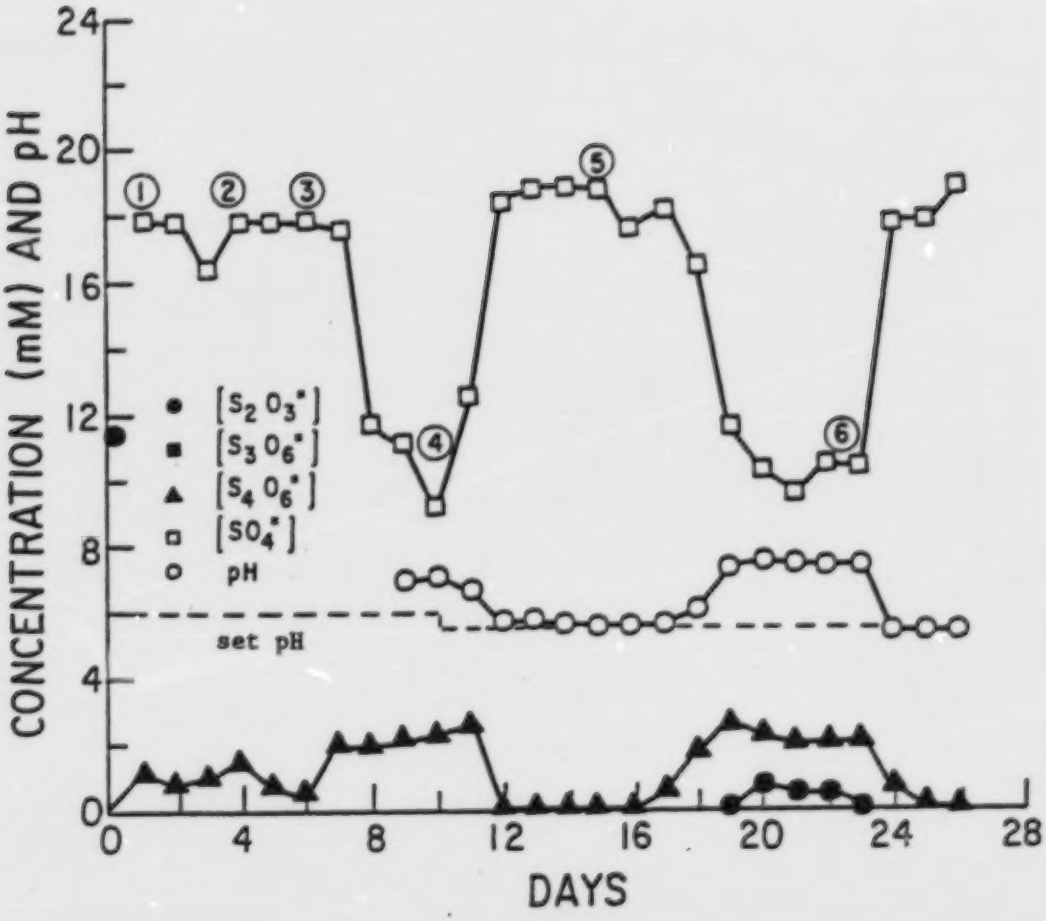


Figure 31. Reactor effluent composition and pH for preliminary synthetic Cu_2S catalyst ($\leq$ 53 μm) continuous run. Catalyst loading = 5 % (w/v), feed solution: 11.5 mM $S_2O_3^=$, 0.5 mM $S_4O_6^=$. Reactor conditions:

1 T = 50°C, feed = 7.0 mL/min, air = 700 mL/min
2 T = 40°C, feed = 7.0 mL/min, air = 700 mL/min
3 T = 40°C, feed = 9.2 mL/min, air = 700 mL/min
4 T = 50°C, feed = 6.3 mL/min, air = 325 mL/min
5 T = 40°C, feed = 6.3 mL/min, air = 325 mL/min
6 T = 50°C, feed = 6.1 mL/min, air = 700 mL/min

to $SO_4^=$ (see Figure 19). A lower reactor temperature reduces the overall oxidation rate, while an increased feed flow reduces reactor residence time; so with these changes there was a higher level of unreacted $S_4O_6^=$ in the reactor effluent.

The pH of the slurry is another factor in determination of the overall oxidation rates. As the temperature was lowered from 50°C to 40°C (days 15 - 23), the pH slowly rose over several days from 5.5 set level to about 7.0 - 7.5. As noted by Chanda et al (11), the overall oxidation rate is lower at higher pH's for Cu_2S catalyst. Since the pH was above the set point, evidently there is a balance between any acid produced by thioanion oxidation (equations (3.1) and (3.6)) and acid consumed (equation (3.5)). This is more apparent for the Converter White Metal run which follows.

When the temperature, feed rate, and air flow rate were reset to the initial values (days 10 - 15, 23 - 26), the conversion to sulfate returned to a high level and the pH dropped to the set level.

Throughout the run, the sulfur balance was somewhat low (about 24 mM sulfur equivalent in feed versus 18 - 23 mM sulfur equivalent in effluent). This was attributed to the formation of insoluble copper hydroxysulfate compounds (see section 4.1.3). There was no detectable copper (< 0.5 ppm) in the effluent.

At the end of the continuous run, a portion of recovered Cu_2S catalyst was reused in a batch experiment. A comparison between the catalytic activity of the "used" Cu_2S and fresh Cu_2S is depicted in Figure 32. There does not seem to be any loss of activity or selectivity to sulfate for the used catalyst.

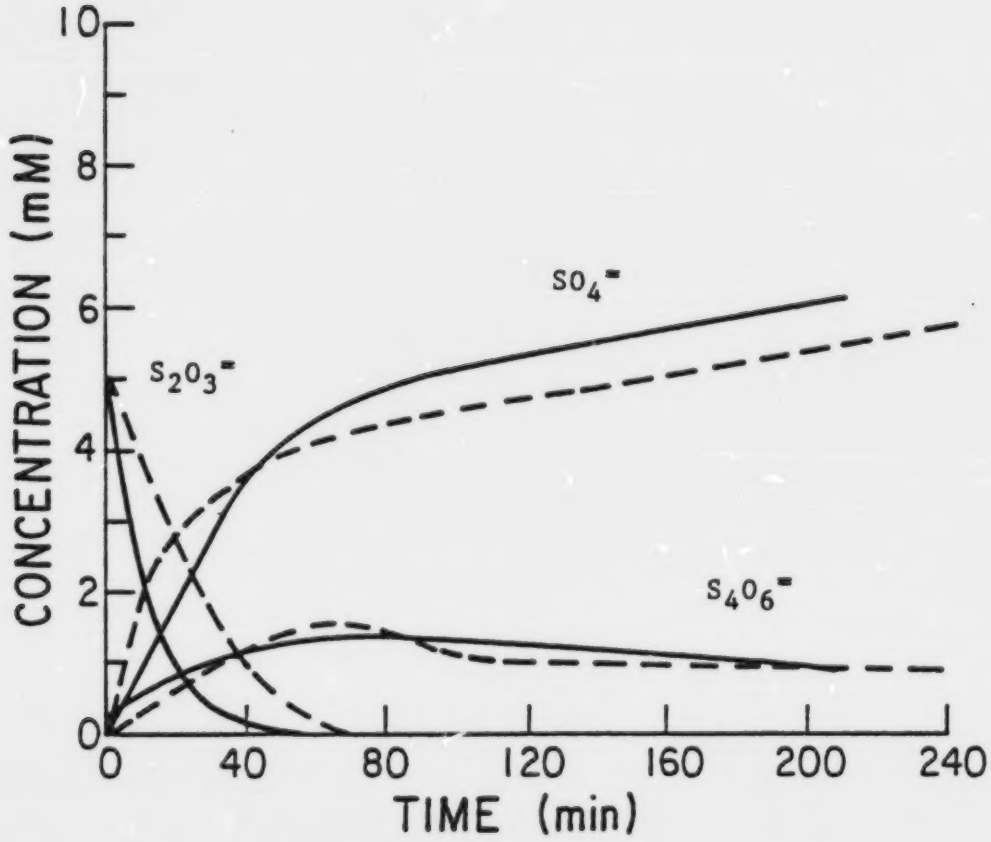


Figure 32. Batch run comparision between fresh Cu_2S catalyst (---) and used Cu_2S catalyst from preliminary continuous run (——). Run conditions: T = 50°C; loading = 5% (w/v); 5.0 mM $S_2O_3^=$ initially.

5.1.3 Converter White Metal catalyst

Data obtained for a Converter White Metal catalyst continuous run over a ten day period is shown in Figure 33. The same reactor conditions which gave good results with Cu_2S catalyst (Figure 31) were used for this run as well (50°C, 6.1 mL/min feed flow, 700 mL/min air flow). A higher catalyst loading was used (7.5 (w/v) % vs. 5 (w/v) %) to compensate for the somewhat lower activity compared to Cu_2S.

As can be seen in Figure 33, the effluent contained mostly $SO_4^=$ (15 - 17 mM), a small amount of $S_4O_6^=$ (0 - 0.5 mM), and no $S_2O_3^=$. However, the sulfur balance was poor (24 mM sulfur in versus 15 - 18 mM sulfur out of the reactor) and the reactor pH stayed at 6.5 - 7.5 throughout the run. Therefore, no caustic was required for neutralization, as the pH set level was 5.5. These observations can be explained in terms of the free copper and cuprite (Cu_2O) present in Converter White Metal catalyst. Acid produced by the oxidation process is readily consumed by these species (thus the pH remains high) and insoluble basic copper sulfates are formed (see section 4.1.3, equations (4.8) and (4.9)). As a result, the effluent $SO_4^=$ concentration is reduced and the overall sulfur balance lowered. X-ray diffraction analysis (see Appendix II) of the used Converter White Metal catalyst collected at the end of the run indicated that both copper and cuprite had been leached out of the catalyst and that the major Cu_2S phase was converted primarily to $Cu_{1.8}S$. However, judging from Figure 33, there was no detectable change in catalyst activity or selectivity throughout the run in spite

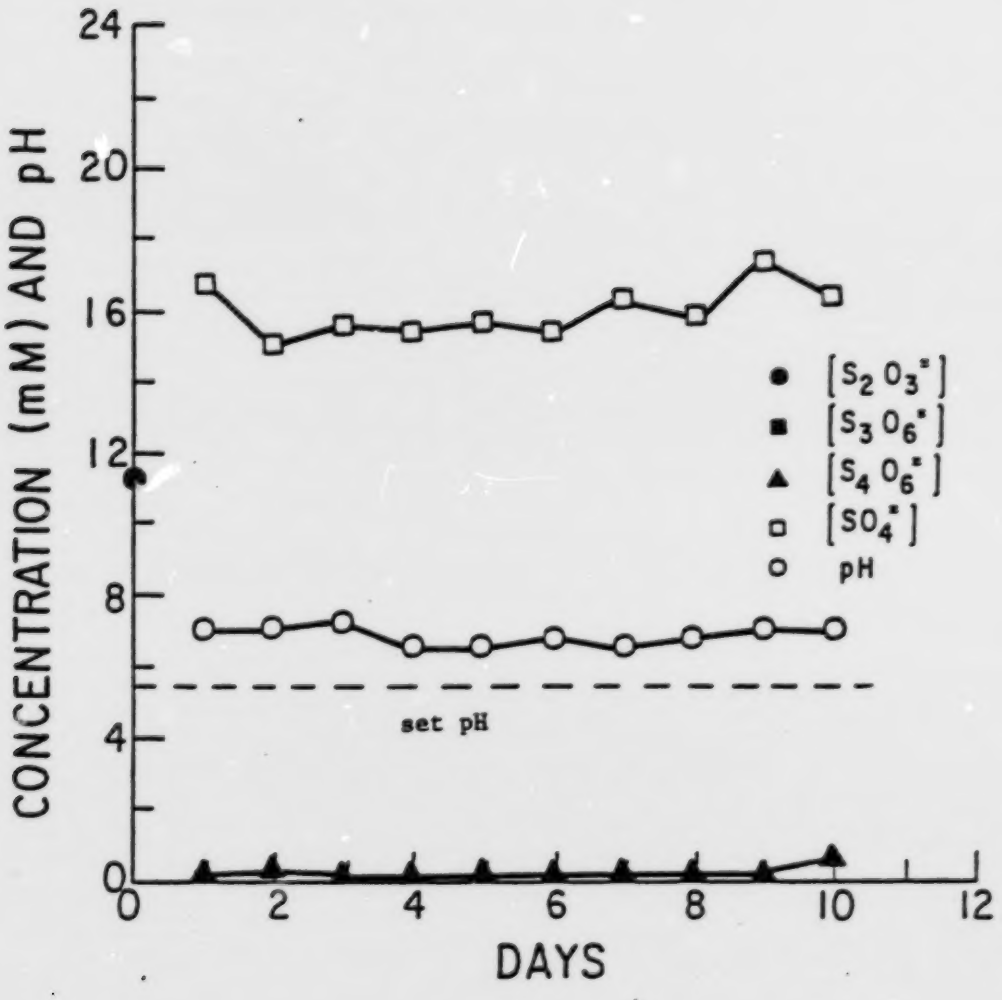


Figure 33. Reactor effluent composition and pH for Converter White Metal catalyst ($\leq$ 53 μm) preliminary continuous run. Reactor conditions: catalyst loading =7.5 % (w/v); T = 50°C; feed flow = 6.1 mL/min; air flow = 700 mL/min; set pH = 5.5 . Synthetic feed composition: 11.5 mM $S_2O_3^=$, 0.5 mM $S_4O_6^=$.

of this change.

5.1.4 Reverbatory Matte catalyst

The results for a 3 1/2 week continuous run with 5 (w/v) % Reverbatory Matte catalyst are shown in Figure 34. The same reactor conditions as used in the Converter White Metal catalyst run (ie. 50°C, 6.1 mL/min feed flow, 700 mL/min air flow) were employed once again.

The Reverbatory Matte catalyst, like Converter White Metal, effectively oxidized the thiosalt feed to $SO_4^=$ (13.5 - 20 mM) and a small residual of $S_4O_6^=$ (0 - 0.5 mM) (see Figure 34). The reactor pH went to the 5.5 setpoint within 48 hours of the start of the run. While the caustic expended to maintain this setpoint was initially low, the consumption rate increased throughout the run as shown in Figure 35. It should be noted that the caustic consumption presented in this figure is on a relative basis ie. the amount of NaOH used is reported as a percentage of the calculated amount that would be required to neutralize H^+ produced by complete oxidation of feed $S_2O_3^=$ and $S_4O_6^=$ to $SO_4^=$ (equations (3.1) and (3.6)). It can be seen from comparison of Figures 34 and 35 that as the relative caustic use increased, the effluent $SO_4^=$ level rose from 14 - 15 mM to 18 - 20 mM. The sulfur balance also improved during this period.

The above results can be interpreted in terms of the limited amount of leachable copper (Cu^+ or Cu) in the Reverbatory Matte catalyst under the acid and oxygen conditions of this study. From Table 4, simple molar proportions give an empirical formula

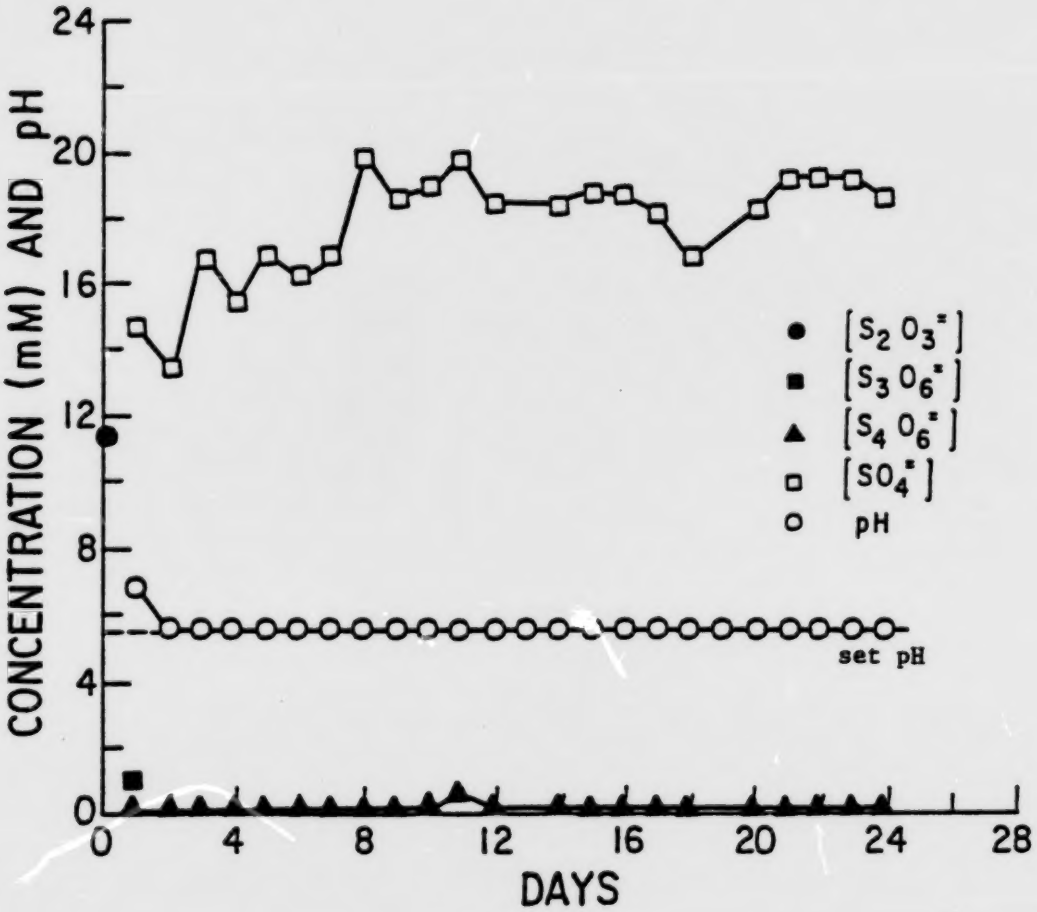


Figure 34. Effluent composition and pH for Reverbatory Matte catalyst ($\leq$ 53 μm) preliminary continuous run. Reactor conditions: catalyst loading = 5 % (w/v); T = 50°C; feed flow = 6.1 mL/min; air flow = 700 mL/min; set pH = 5.5 . Synthetic feed composition: 11.5 mM $S_2O_3^=$; 0.5 mM $S_4O_6^=$.

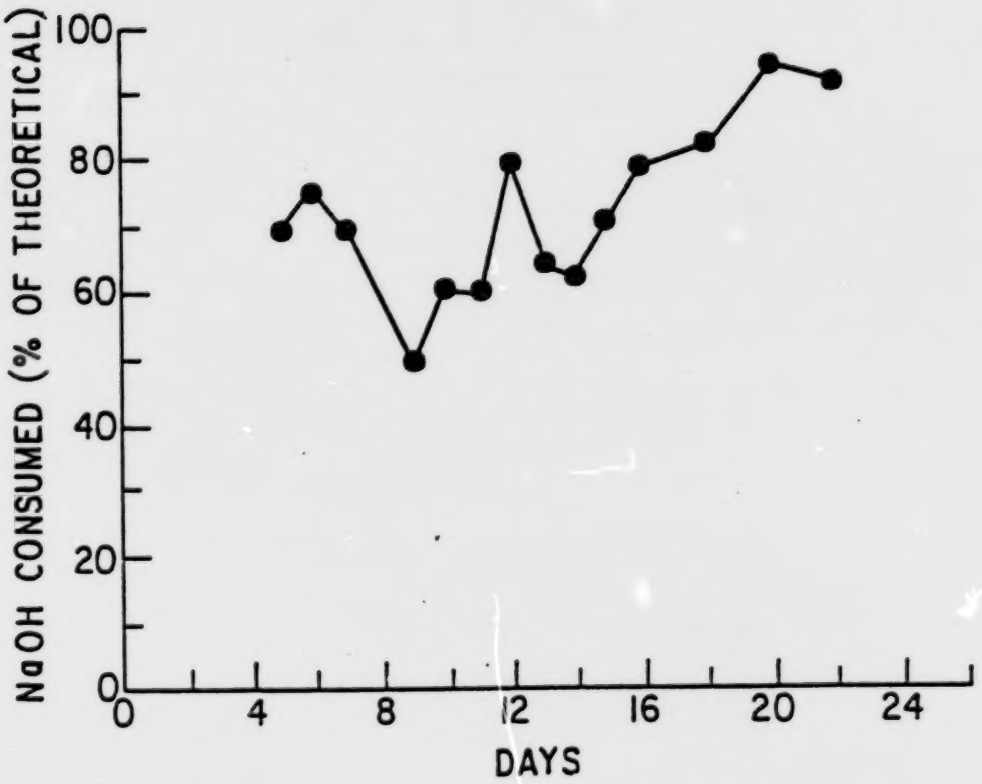


Figure 35. Percent of theoretical NaOH consumed in preliminary Reverbatory Matte catalyst run vs. days into run. Theoretical NaOH is the calculated amount necessary to neutralize H^+ from complete oxidation of feed thioanions to sulfate by overall reactions (3.1) and (3.6).

of $Cu_{0.61}Fe_{0.27}S_{1.0}$ or $(Cu,Fe)_{0.9}S_{1.0}$ for Reverbatory Matte, which indicates a preponderance of Cu^{2+}. Specific compounds $(Cu,Fe)_{1.01}S_{1.0}$ and $Cu_{2.9}Fe_{1.0}S_{2.7}$ were also identified by X-ray diffraction (Appendix II). Therefore, very little of the acid produced by thiosalt oxidation is used up in oxidative catalyst degradation (hence more caustic is needed for neutralization) and the formation of basic copper sulfate compounds is correspondingly reduced. As a result, the effluent $SO_4^=$ level increases and the sulfur balance improves. As a further check on the mass balance, the amount of basic copper sulfate formed in the reactor was determined by extraction of a portion of the reactor catalyst with 10 % HCl under anaerobic conditions. The resulting leachate was analyzed for both $SO_4^=$ and Cu^{2+} (see Table 12) and the total insoluble sulfate within the reactor calculated. Addition of this amount to the total effluent sulfur equivalent accounted for about 80 % of the sulfur equivalent fed to the reactor over the same time period.

It is of interest to compare the results of the Converter White Metal and Reverbatory Matte continuous runs. Both of these catalysts seem equally effective in oxidation of thiosulfate and tetrathionate to sulfate under the same conditions (except for pH), yet the predominant phase in Converter White Metal is Cu_2S while Reverbatory Matte is much closer to (Cu,Fe)S. However, CuS shows very little catalytic activity (see oxygen uptake experiments, section 3.1). It appears that although the catalyst composition might change with time by oxidative acid decomposition ($Cu_2S \longrightarrow Cu_{1.96}S \longrightarrow Cu_{1.8}S \longrightarrow Cu_{1.1}S$), activity is not appreciably affected until the catalyst obtains a CuS

Table 12. Analysis of acid leachate of Reverbatory Matte catalyst samples taken on days 7 & 8 from preliminary Reverbatory Matte catalyst run (Figure 34) and calculated sulfur balance.

catalyst sample	sample weight (gm)	moles $SO_4^=$ in leachate x 10^3	moles Cu^{2+} in leachate x 10^2	moles Cu^{2+}/ moles $SO_4^=$ (1)	moles $SO_4^=$ in reactor (2)	moles S fed to reactor (A)	moles S (in effluent + in reactor) (B)	sulfur balance (B)/(A) x 100
day 7(3)	17.75	7.31	1.33	1.85	0.206	1.475	1.210	82
day 8(4)	24.62	8.75	3.77	4.33	0.178	1.658	1.321	80
"unused" catalyst (4)	25.0	0	not analyzed	-	-	-	-	-

(1) expected $Cu^{2+}/SO_4^=$ for "brochantite" [$CuSO_4.3(Cu(OH)_2)$] is 4.00

(2) based on 500 grams of catalyst in reactor

(3) stirred with 10 % HCl for 30 minutes

(4) stirred with 10 % HCl for 3 hours

composition. This supposition is explored further in section 5.3.2.

5.2 Converter White Metal - Extended Runs

The preliminary run results were presented in an interim report (28) and discussed with Dr. J. Dutrizac (CANMET) at a meeting at the University of Waterloo (June 11, 1984). This meeting was called to evaluate the first six months of this study and to provide direction for the final six months of project work. It was decided that, in view of time limitations imposed by carrying out long continuous runs, future work should concentrate on only one catalyst. Converter White Metal was chosen because of its initial good performance for thioanion oxidation and ready availability. The development work was to focus on using higher catalyst loadings and lower temperatures in order to obtain information that might be useful in assessing the economic feasibility of a thioanion oxidation process using Converter White Metal. Also, while simple synthetic solutions of sodium thiosulfate chosen for the preliminary runs were useful for catalyst characterization, more realistic feeds would have to be employed. Therefore, several runs were carried out with particular attention to the following parameters and/or conditions:

(a) Addition of Zn^{2+}, Pb^{2+}, and Ag^{+} (22, 5.3, and 3.5 ppm respectively) to synthetic feed, since these metal ions are normally present in thiosalt effluents.

(b) Dramatic changes in thiosalt concentration to simulate

a "surge" in the feed (this aspect appears troublesome in biological oxidation processes for thioanions).

(c) 30 (w/v) % slurry loading and 30°C reaction temperature. Mill wastewater is normally 30°C or less.

(d) Examination of more realistic synthetic feeds containing higher polythionate levels and Fe^{2+}.

Finally, a few runs using real mining thiosalt wastewater obtained from Brunswick Mining and Smelting were felt to be desirable.

A PVC reactor was constructed (see Experimental section 2.2.1) and used for this phase of the work because of corrosion problems experienced with the stainless steel reactor employed for the preliminary reactor studies. For the 30 (w/v) % slurry loading experiments, a PVC reactor-settler setup was utilized (see Figure 7).

5.2.1 Effect of Zn^{2+}, Pb^{2+}, and Ag^{+} and Surge in Thiosalt Feed Concentration

The Converter White Metal catalyst recovered from the preliminary run (section 5.1.3) was reused in this experiment. The catalyst loading was decreased to 5 (w/v) %, but other reactor conditions were the same as in the preliminary run. The reactor effluent analytical results collected over a 30 day run period are shown graphically in Figure 36.

As in the preliminary run, reactor pH remained above the 5.1 setpoint with an 11.8 mM $Na_2S_2O_3$ feed (see Figure 36, days 1 - 5) and the effluent contained mostly $SO_4^{=}$ (12.5 - 13 mM) with a

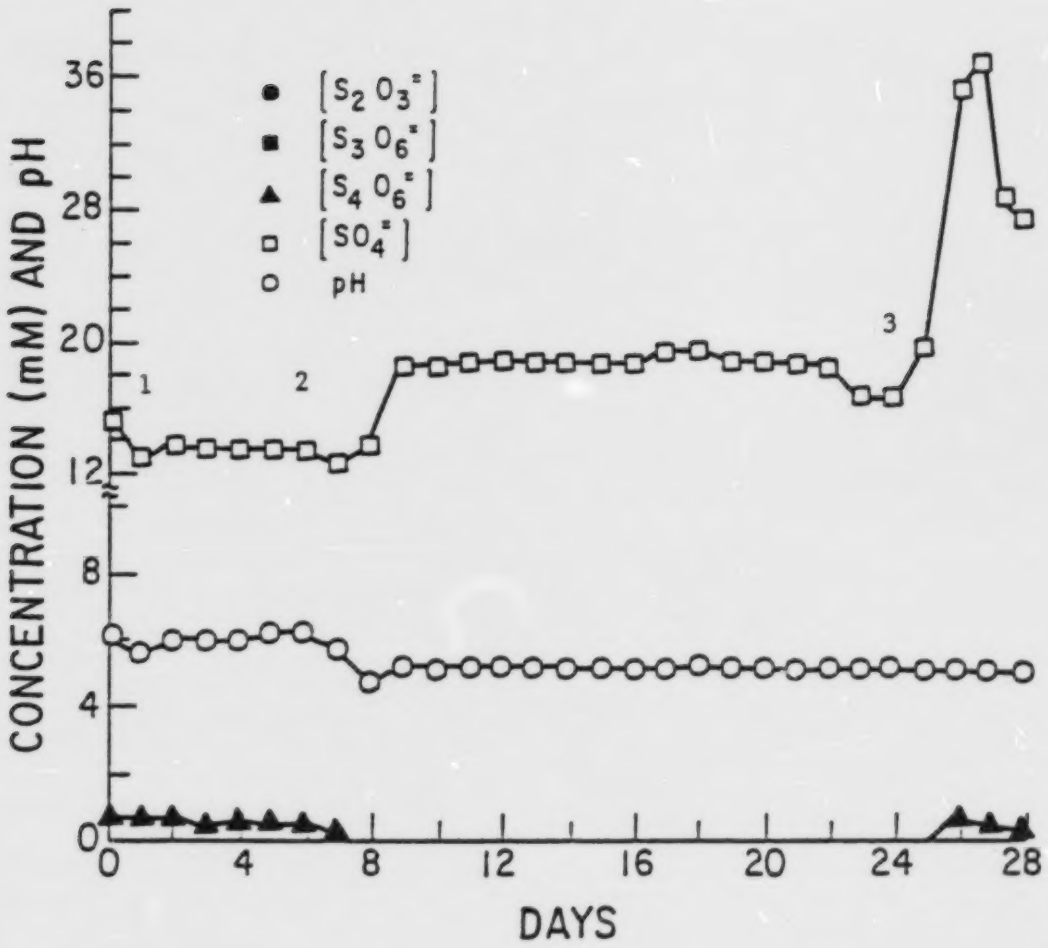


Figure 36. Reactor effluent composition and pH for continuous run with used Converter White Metal catalyst from preliminary experiment (section 5.1.3). Reactor conditions: catalyst loading = 5 % (w/v); T = 50°C; feed flow = 6 mL/min; air flow = 700 mL/min; set pH = 5.1 . PVC reactor apparatus used.
Feed composition: 1 11.8 mM $S_2O_3^=$

2 21.9 ppm Zn^{++}, 5.3 ppm Pb^{++}, 3.5 ppm Ag^+ added

3 18 mM $S_2O_3^=$

small $S_4O_6^=$ residual (about 0.5 mM). However, when Ag^+ (3.5 ppm), Pb^{2+} (5.3 ppm), and Zn^{2+} (21.9 ppm) were added to the feed on day 6, the pH dropped to the set level, effluent $SO_4^=$ quickly rose to 18 - 19 mM, and the $S_4O_6^=$ residual disappeared. It would seem that these metal ions inhibit the oxidative acid leaching of the copper sulfide catalyst and perhaps increase activity, although the reason for this effect is not clear.

When the thiosulfate feed concentration was raised from 11.8 to 18 mM (days 24 - 28), the effluent $SO_4^=$ increased sharply to 32 - 34 mM. This was essentially stoichiometric oxidation of the feed to $SO_4^=$, although this conversion dropped off after a few days (days 27, 28). A small $S_4O_6^=$ residual (0.3 mM) reappeared during this period, but $S_2O_3^=$ was not detectable.

In Figure 37, the amount of NaOH used for neutralization (as a percentage of the theoretical amount calculated for neutralization of acid from equations (3.1) and (3.6)) and the residual copper in the effluent are plotted for the 28 day run. Initially, no caustic was required (pH was above setpoint), however when Zn^{2+}, Pb^{2+}, and Ag^+ were added to the feed the caustic consumption rose sharply to 70 - 90 % of the theoretical requirement. This is due to decreased acid consumption by oxidative catalyst decomposition, as the metal ions seem to inhibit this reaction. Thus more free acid must be neutralized. It is also of interest to note that the soluble copper increased from non -detectable levels to 70 - 80 ppm during this same period; this rise cannot be explained by the decrease in pH (6 to 5.1) alone. As the feed $S_2O_3^=$ concentration increased from 11.8 to 18 mM (day 25), the relative NaOH usage dropped off to about

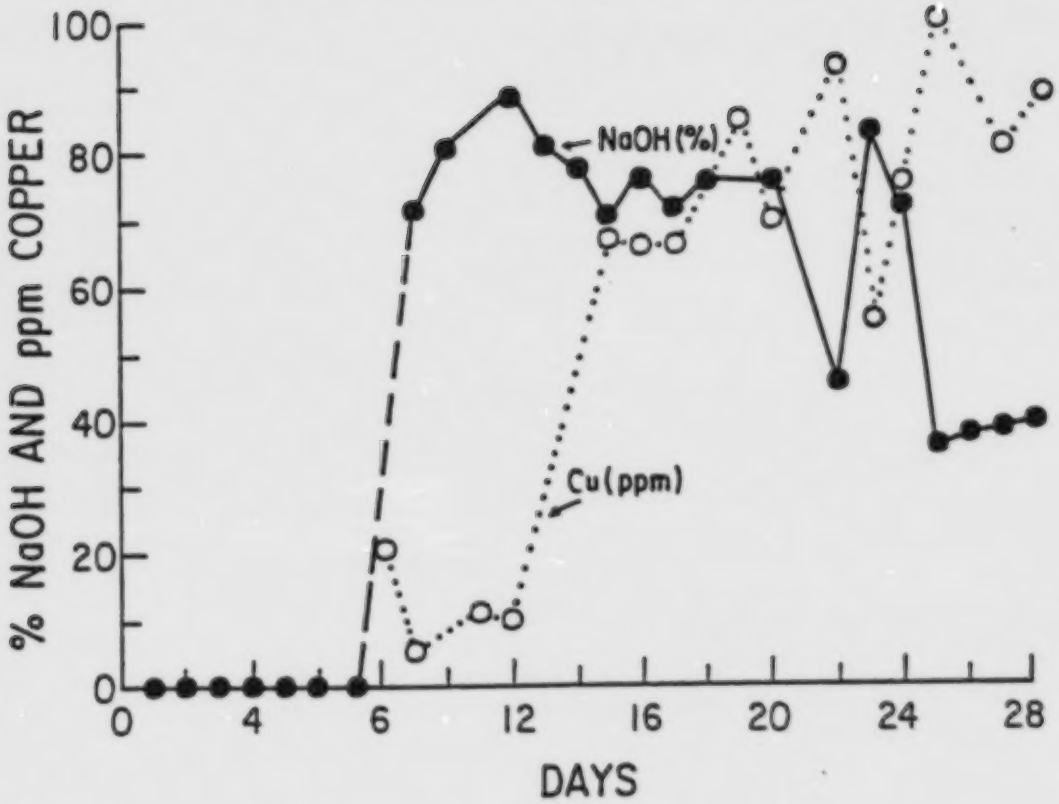


Figure 37. Percent of theoretical NaOH consumed and soluble effluent copper (ppm) for Converter White Metal catalyst run (Figure 36). Theoretical NaOH consumption based on total oxidation of feed thioanions to sulfate by reactions (3.1) and (3.6).

40 % of the theoretical requirement after a few days. The reason for this decrease is not clear.

5.2.2 High Slurry Loading (30 w/v %) and Low Temperature (30°C) run - Effect of Fe^{++} and pH

Continuous experiments reported in sections 5.1.2 to 5.2.1 involved 5 to 7.5 (w/v) % slurry loadings at reaction temperatures of 40° - 50°C. In order to assess the Converter White Metal catalyst under more practical conditions, experiments were carried out with much higher loadings (30 (w/v) %) at 30°C. The high loading is more typical of slurry reactor processes, and the mining effluent thiosalt effluent temperature is 30°C or less at discharge.

A run made using these parameters is shown in Figure 39. In addition to the above changes, the air flow rate was reduced to 150 - 300 mL/min (about 5 to 10 times theoretical amount of oxygen necessary for complete oxidation of thiosalts), and feed flow increased to 12.4 mL/min, thus reducing reactor residence time from about one day to 13 hours. Fresh Converter White Metal catalyst was used and the feed contained, besides $Na_2S_2O_3$ (12 - 14 mM), Pb^{2+} (21.9 ppm), Zn^{2+} (5.3 ppm), and Ag^{+} (3.5 ppm), added $S_4O_6^{=}$ (1 - 3 mM as $K_2S_4O_6$) and Fe^{2+} (50 ppm, as $FeSO_4$). Also, the feed pH was adjusted to between 3 - 5.5 with added sulfuric acid. The feed thioanion composition and pH over the 26 day run are shown in Figure 38. At the lowest pH, $S_3O_6^{=}$ was formed in the feed; the mechanism for this is not clear.

In this run, the variation in reactor pH was studied, as this parameter is known to have a significant effect (see section

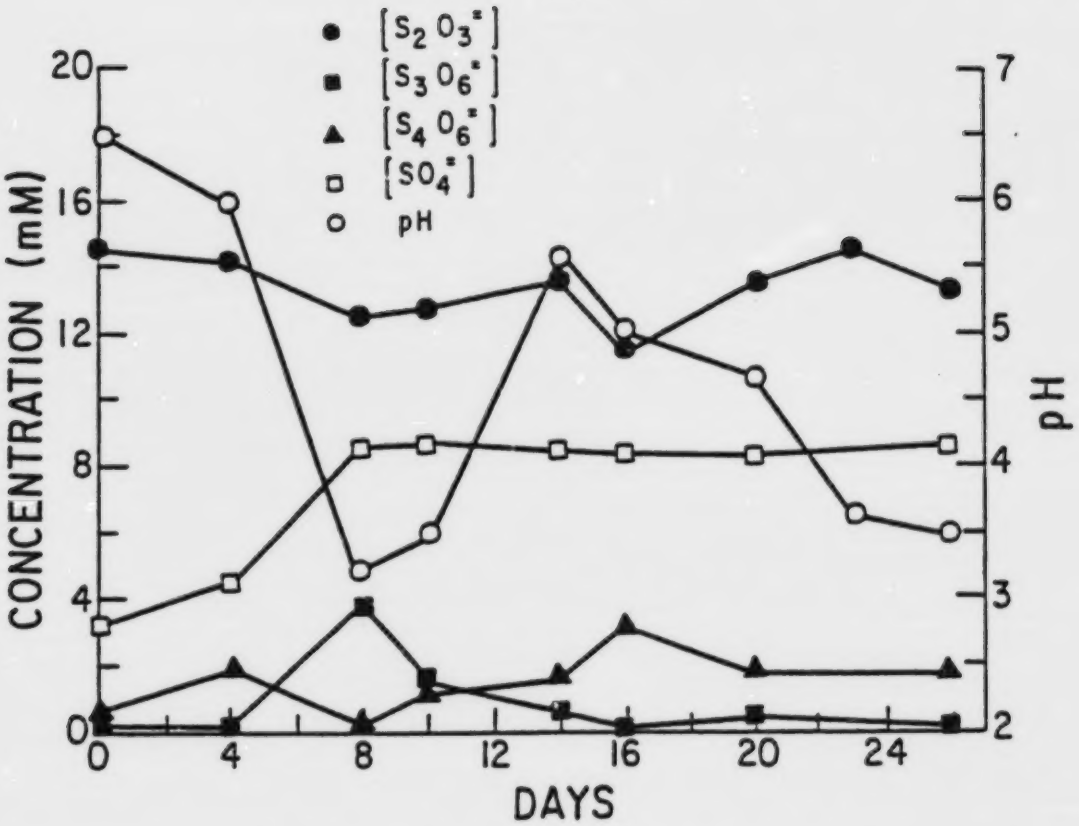


Figure 38. Feed composition and pH for high slurry loading Converter White Metal catalyst continuous run shown in Figure 39.

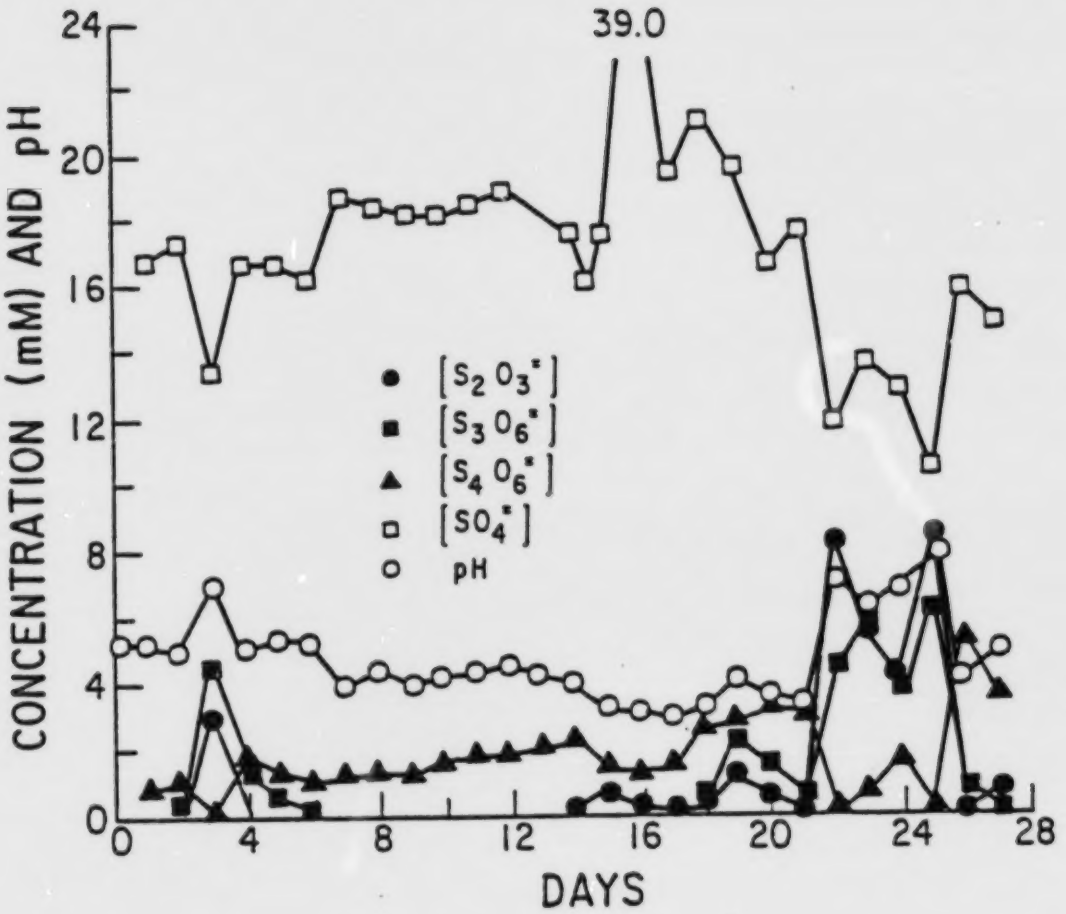


Figure 39. Reactor effluent composition and pH for high loading Converter White Metal catalyst run. Reactor conditions: catalyst loading = 30 % (w/v); T = 30°C; feed flow = 12.4 mL/min; air flow = 150 to 300 mL/min; pH was variable: 5.5 (days 1-5), 4-4.5 (days 6-14), 3-4 (days 15-21), 5-8 (days 22-27). Sulfuric acid added to lower pH on days 15-21 . PVC reactor/settler apparatus used.

4.1.3). Initially, the pH was 5.5 (see Figure 39, days 1 - 5. On day 3, the feed pump malfunctioned and ran at a high rate). The conversion to $SO_4^=$ was reasonably good (15 - 17 mM), but there was significant amounts of $S_4O_6^=$ (1 mM) and some $S_3O_6^=$ produced. A buildup of dirt-brown precipitate, presumably $Fe(OH)_3$, was noticed in the reactor. As the pH was lowered to 4 - 4.5 (days 6 - 14), the effluent $SO_4^=$ level increased slightly (18 - 19 mM) and $S_4O_6^=$ levels increased as well (1 - 2 mM). Although the higher $S_4O_6^=$ concentration can be attributed to a lower catalyst activity, a more probable explanation is that more $S_4O_6^=$ is made within the reactor from oxidation of $S_2O_3^=$ by Fe^{2+}/O_2, ie.

$$2\ Fe^{2+} + 0.5\ O_2 + 2\ H^+ \longrightarrow 2\ Fe^{3+} + H_2O \qquad (5.1)$$

$$2\ Fe^{3+} + 2\ S_2O_3^= \longrightarrow S_4O_6^= + 2\ Fe^{2+} \qquad (5.2)$$

At higher pH's (>5), the thiosulfate oxidation reaction (5.2) is suppressed since Fe^{+3} is insoluble as the hydroxide.

In order to lower the reactor pH still further to 3 - 4 (days 15 - 21), it was necessary to add sulfuric acid using the pH meter/controller. The lower pH greatly accelerates the acid decomposition of the catalyst and a considerable amount of H_2SO_4 was required to maintain these low pH levels (Table 13). The effluent $SO_4^=$ increased substantially from the added acid and dissolution of previously precipitated basic copper sulfate compounds. While a higher catalyst activity was expected at this low pH, the $S_4O_6^=$ level did not change substantially and unreacted $S_2O_3^=$ appeared in the effluent; this indicated a lower

activity. When the reactor pH was raised to 6.5 - 8 (days 22 - 27), it was apparent that the activity had dropped off considerably. The $S_2O_3^=$ and $S_3O_6^=$ concentrations were quite high (4 - 8 mM and 4 - 7 mM, respectively) and very little additional $SO_4^=$ was produced (ie. the feed and effluent $SO_4^=$ levels remained about the same). A high concentration of $S_3O_6^=$ was evident, probably due to the basic decomposition of $S_4O_6^=$ (equation (4.3)) which is reportedly catalyzed by $S_2O_3^=$ (29).

Table 13. Sulfuric acid added to control reactor pH for Converter White Metal catalyst continuous run (Figure 39). *

Time period	H_2SO_4 added mL	H_2SO_4 added concentration	H_2SO_4 added (moles)
day 15 - 16	86	9M	1.62
day 16 - 18	30	1M	0.06
day 18 - 19	35	1M	0.07
day 19 - 20	40	1M	0.08
day 20 - 21	13	1M	0.03
			total = 1.86 moles

* Total cumulative moles H_2SO_4 generated from oxidation of thiosalts by day 22 = 2.80.

Even after several days, catalyst activity was not restored and the run was stopped. The spent catalyst had the dark blue colour characteristic of CuS (covellite); thus, the loss of activity presumably was due to rapid decomposition of Cu_2S to CuS at pH 3. It is also worth noting that the sulfur mass balance was quite good for this deactivated Converter White Metal catalyst, as the possibility of forming basic copper sulfates with a material consisting primarily of CuS is negligible.

In Figure 40, the effluent soluble copper and iron levels for this run are shown. At the beginning of the run, the pH was

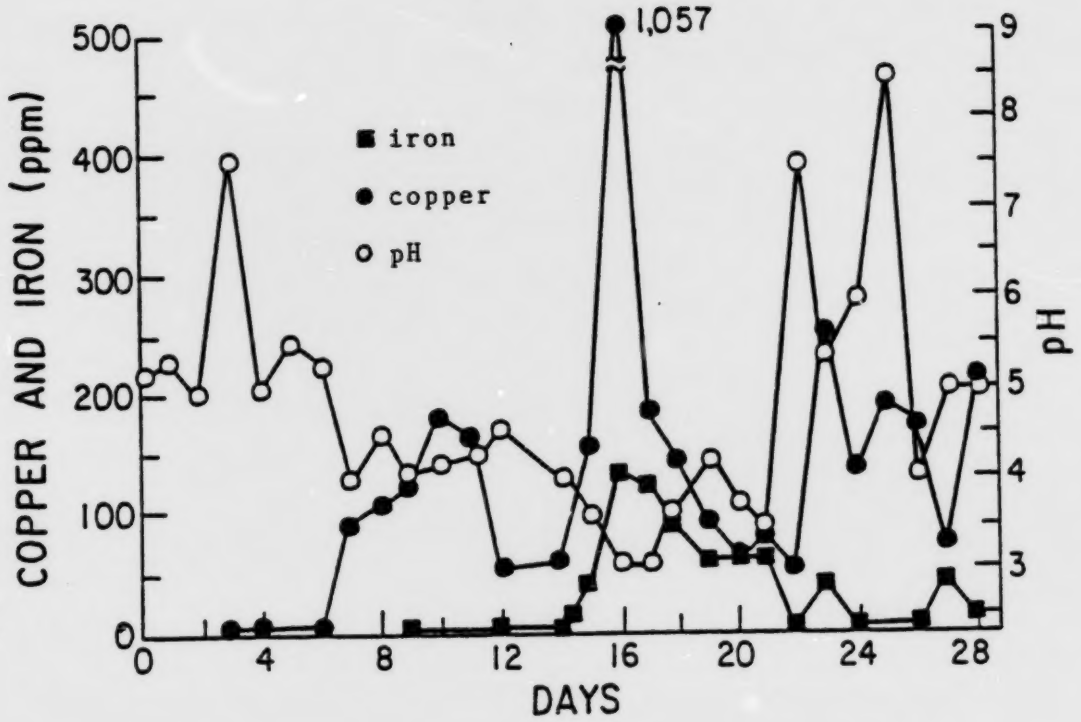


Figure 40. Soluble effluent copper and iron (ppm) and reactor pH for Converter White Metal catalyst run depicted in Figure 39.

relatively high (ie. > 5) and both copper and iron were insoluble as the basic sulfate and hydroxide respectively. However, as the pH was lowered to 4 - 4.5, copper was solubilized from dissolution of basic copper sulfate (see also Figure 22). As the pH was lowered still further to 3 - 4, catalyst decomposition became appreciable and the amount of soluble copper increased dramatically. In this same pH region, accumulated iron hydroxide begins to dissolve. When the pH was increased to 5 - 8 (days 23 - 28), both copper and iron levels were reduced somewhat, but were still quite high compared to previous operation in this pH region (days 1 - 5).

The results in this run indicate that a reactor pH of 4 or higher should be maintained in order to avoid excessive catalyst decomposition. Yet at these higher pH's, ferric hydroxide buildup in the reactor becomes a ever increasing problem.

5.2.3 High Slurry Loading (30 w/v %) and Low Temperature (30°C) Run - Synthetic Feed with added Trithionate

In addition to thiosulfate and tetrathionate, trithionate represents another serious pollutant present in mining wastewater. In previous runs (sections 5.1.1 to 5.2.2), $S_3O_6^=$ was produced at low levels by conversion of $S_2O_3^=$ and $S_4O_6^=$, but there was no clear indication of further oxidation of the resulting $S_3O_6^=$ to $SO_4^=$, although this seemed to be the case in batch experiments (section 4.1.1 and Figure 17). Thus, the addition of trithionate to the synthetic feed was considered pertinent with respect to the overall destruction of thioanions by Converter White Metal.

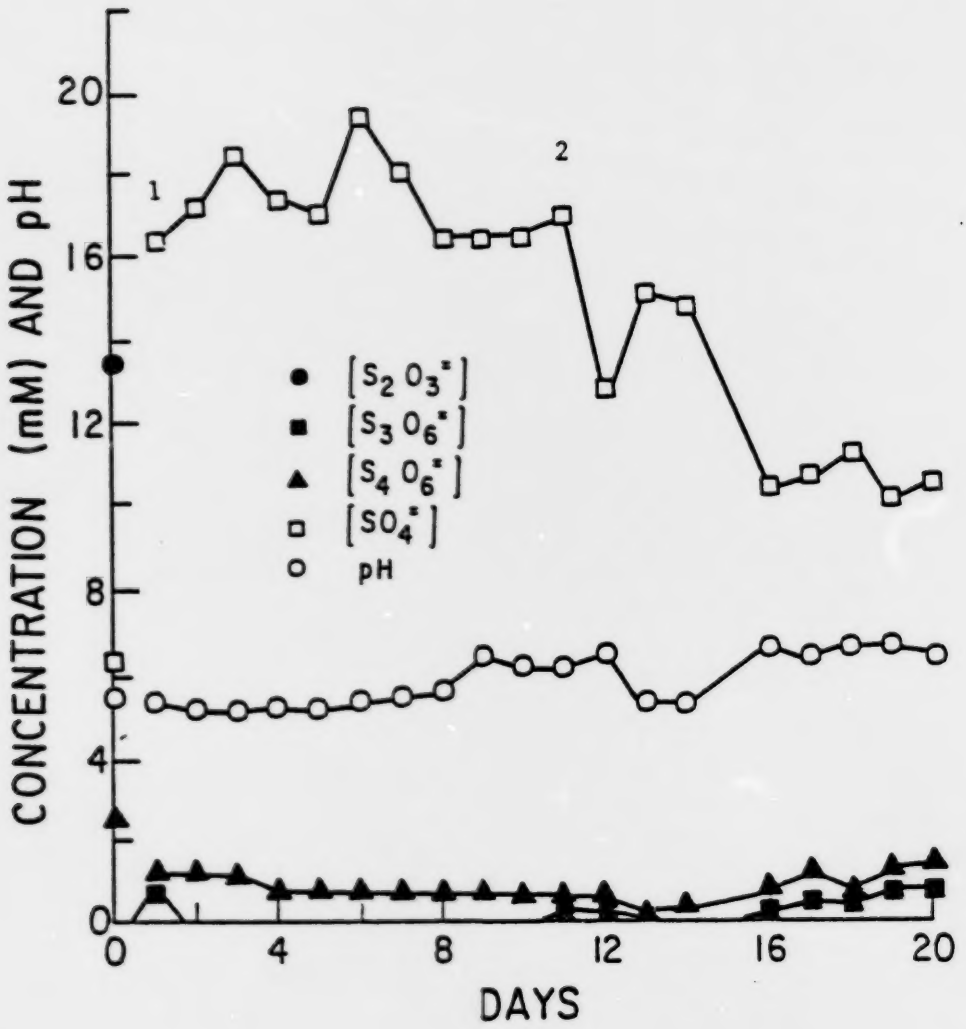


Figure 41. Reactor effluent composition and pH for Converter White Metal catalyst continuous run with trithionate added to feed. Reactor conditions: catalyst loading = 30 % (w/v); T = 30°C; feed flow = 12 mL/min; air flow = 300 mL/min; set pH = 5.0.
Feed composition:

1 14.3 mM $S_2O_3^=$, 1.5 mM $S_4O_6^=$, and 50 ppm Fe^{++}, 21.9 ppm Pb^{++}, 5.3 ppm Zn^{++}, and 3.5 ppm Ag^+.

2 8.5 mM $S_2O_3^=$, 1.5 mM $S_4O_6^=$, 1.0 mM $S_3O_6^=$, added metal ions as for feed composition 1.

The effluent data collected for a 30 (w/v) % Converter White Metal catalyst slurry, 30°C run is shown in Figure 41. During the initial period (days 1 - 10), the feed consisted of $S_2O_3^=$ (14.3 mM), $S_4O_6^=$ (1.5 mM), Fe^{2+} (50 ppm), Pb^{2+} (21.9 ppm), Zn^{2+} (5.3 ppm), and Ag^+ (3.5 ppm). On day 11, the feed was changed to 8.5 mM $S_2O_3^=$, 1.5 mM $S_4O_6^=$, 1.0 mM $S_3O_6^=$; and the added metal concentrations remained the same. All other reactor parameters were kept the same, although pH was allowed to fluctuate freely in the early part of the run.

With only $S_2O_3^=$ and $S_4O_6^=$ present in the feed , the effluent composition was similar to previous runs (sections 5.3.1 to 5.3.2) under the same conditions, although the residual $S_4O_6^=$ was somewhat higher (1 mM). The reactor pH remained more or less constant during this period (5.1 - 5.6). When $S_3O_6^=$ was added to the feed (day 11), the pH level increased to 6 - 6.5, and some unreacted $S_3O_6^=$ was detected in the effluent (0.3 mM). On day 13, 1M H_2SO_4 was metered into the reactor to maintain a pH of 5.2. With the lower pH, both $S_4O_6^=$ and $S_3O_6^=$ levels dropped, presumably from higher catalyst activity. When acid addition was stopped (day 14), the reactor pH rose to near neutrality (6.5 - 6.9) and $S_4O_6^=$ and $S_3O_6^=$ levels rose as well (1.3 mM and 0.9 mM, respectively), while the $SO_4^=$ concentration dropped accordingly to 10 - 11 mM. In fact, the $S_3O_6^=$ feed and effluent levels were essentially the same.

The above results confirm batch data (section 4.1.2) in that $S_3O_6^=$ was not destroyed at pH of 7 or above, but was oxidized below this pH. However, the rate of oxidation at lower pH's was much slower than that observed in the batch experiments

(Figure 17) where only a few minutes were necessary to destroy $S_3O_6^=$ at pH 7 or less.

5.2.4 Brunswick "Tailings Decant" Wastewater - Run #1

Since continuous thioanion oxidation of synthetic feed solutions with Converter White Metal catalyst was moderately successful, additional work was undertaken using real mining effluent. A 200 L barrel of "Tailings Decant" (from Brunswick Mining and Smelting, New Brunswick) was obtained through CANMET. This material contained relatively low concentrations of thioanions (see Table 14 below); normally this solution is mixed with "thickener overflow" to give the total wastewater composition. Unfortunately, none of the latter was received due to problems in shipment.

Table 14. Composition of Brunswick Mining and Smelting "Tailings Decant" water used in Continuous Runs # 1 and # 2 (Figure 42).

Component	Run # 1 "Tailings Decant"	Run # 2 "Tailings Decant"
$S_2O_3^=$, mM	5.01	3.08
$S_3O_6^=$, mM	0.62	0.58
$S_4O_6^=$, mM	0.39	0.49
$SO_4^=$, mM	22.0	17.8
Fe^{++}, ppm	105	488
Ca^{++} or Mg^{++}, mM	13.4	12.2
Cu^{++}, ppm	nil	nil
pH	6.5	6.1

The tailings decant wastewater was fed to the continuous reactor over a 9 day period. The thioanion composition of the effluent over the entire run period is shown in Figure 42. Because the thiosalt level was quite low (5 mM), the feed rate was somewhat higher than previous runs with synthetic solutions (15 mL/min versus 12 mL/min).

The results obtained are consistent with the continuous experiments for synthetic feed solutions. Thiosulfate was reduced to non-detectable levels and $S_4O_6^=$, $S_3O_6^=$ were also reduced slightly. However, the effluent $SO_4^=$ concentration remained about the same as the feed. It was noticed that as the run proceeded, a "slimy" green-brown precipitate built up in the reactor-settler apparatus. Also, the effluent contained essentially no soluble iron (< 1 ppm) whereas the feed contained 105 ppm Fe^{2+}. A simple 10 % HCl acid extraction of a small amount of catalyst/precipitate gave evidence of Cu^{2+}, Fe^{3+}, and $SO_4^=$. It seems likely that the green-brown precipitate is a combination of basic copper sulfate and ferric hydroxide. This material tended to suspend catalyst particles, and so caused increasing problems in the settler apparatus. However,the precipitate did not seem to lower catalyst activity.

The initial reactor pH was 5.4, but this rose steadily to 8 by day 6. On day 7, 1M H_2SO_4 was metered in to lower the reactor pH to 4. At this lower pH, $S_3O_6^=$ and $S_4O_6^=$ were reduced to nondetectable levels.

The available supply of tailings decant wastewater was exhausted at the end of the 9^{th} day, and consequently the run had to be terminated.

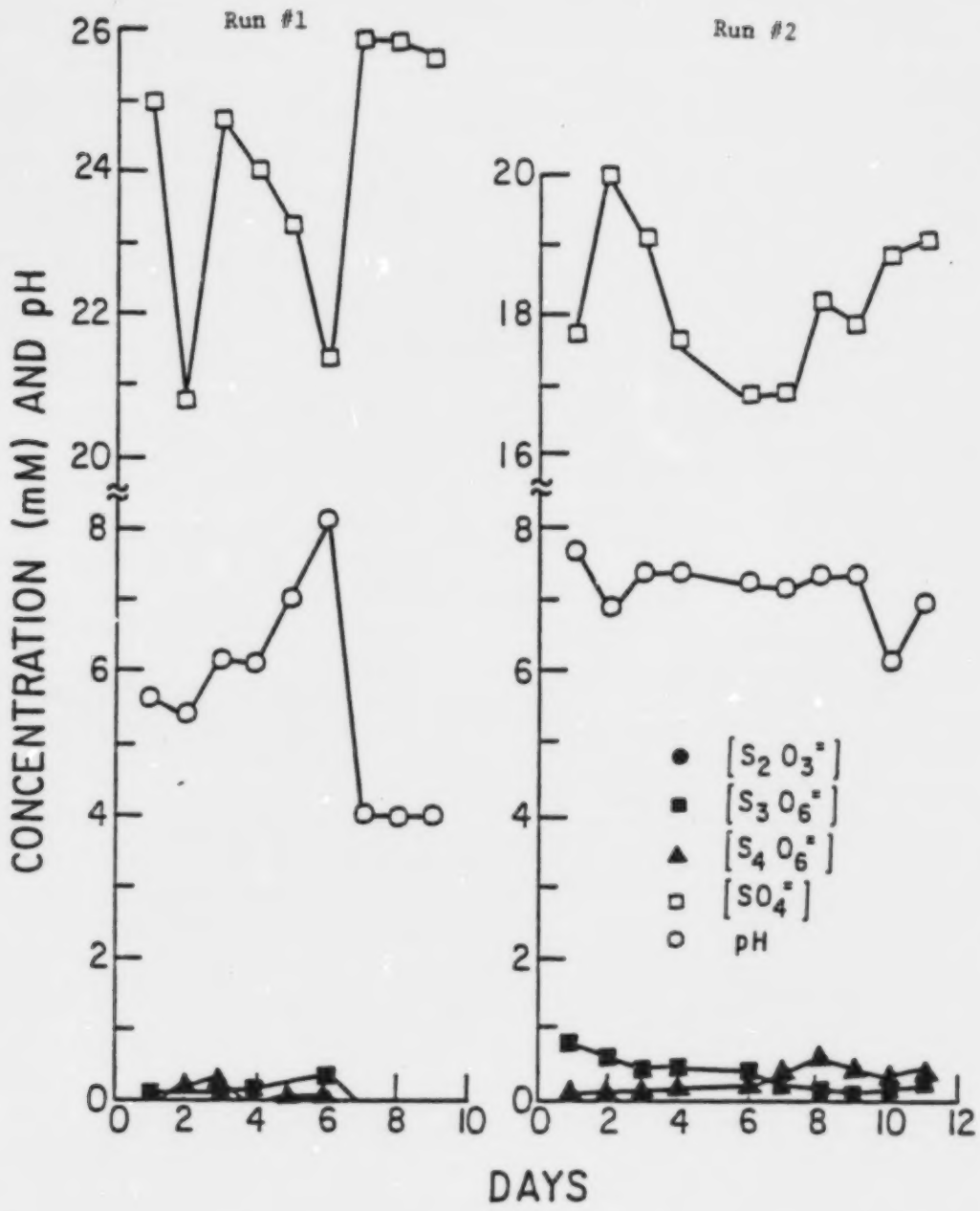


Figure 42. Effluent composition and pH for " Tailings Decant" wastewater feed runs #1 and #2. Reactor conditions: Converter White Metal catalyst (≤ 75 um) 30 % (w/v); T = 30°C; feed flow = 15 mL/min; air flow = 350 mL/min. Sulfuric acid (1M) added to lower pH in run #1, days 7-9 .

5.2.5 Brunswick "Tailings Decant" Wastewater - Run # 2

An additional two barrels (200 L each) of Brunswick Mining and Smelting tailings decant water was received for further tests. This material was somewhat lower in thiosulfate (3.1 mM versus 5.0 mM) and had a much higher iron content (488 ppm versus 105 ppm) than the previous material (see Table 14, Run # 2).

The effluent results for an eleven day run (see Figure 42) were similar to those in the first run. New catalyst was employed for this run and the reactor conditions were the same as those used for Run # 1 (Figure 42 (a)). Again thiosulfate was reduced to non detectable levels, however, probably due to the higher overall reactor pH (6 - 7.5), $S_4O_6^=$ and $S_3O_6^=$ were not significantly reduced from feed levels. The effluent $SO_4^=$ concentration was again approximately equivalent to the untreated "Tailings Decant" levels.

The buildup of $Fe(OH)_3$ floc in the reactor was much more of a problem than in the first run due to the much higher Fe^{2+} concentration in the wastewater for Run # 2. At the end of the run (day 11), the iron hydroxide - coated Converter White Metal catalyst was essentially unusable in the apparatus, as it would not settle properly although, as noted in Run # 1, there was no evidence the precipitate caused any decrease in catalyst activity.

6. CONCLUSIONS

As discussed in the introduction, the statement of work was divided into two phases.

6.1 Phase I

1) Sixteen ore concentrates obtained for CANMET were evaluated with respect to their catalytic activity for thiosalt oxidation using an oxygen uptake apparatus.

Two of the catalysts showing the greatest initial rates of oxygen consumption were chosen for further study: Reverbatory Matte and Converter White Metal.

2) The two preferred sulfides were investigated in some detail using both a gas uptake and batch apparatus in order to identify the optimum operating parameters.

6.1.1 Gas Uptake Experiments

Operation of Reactor

a) In order to eliminate settling of the catalyst and mass transfer problems, a shaking speed of 200 rpm or greater is desirable.

b) The initial rate was found to be proportional to the catalyst loading. However, at high catalyst loadings (1/loading ---> 0), the rate was found to be limited by the transfer of O_2 at the gas-liquid interface. Consequently, a 4 (w/v) % loading was used to avoid these problems in the present study.

c) A particle size of less than 45 μm is desirable in order to increase the catalyst's surface area exposed to the reaction

solution.

d) Acetate and phosphate buffers were examined for use as the reaction medium in order to keep the pH constant throughout the experiment. The acetate buffer caused considerable leaching of the copper, as copper acetate, into solution. The phosphate buffer demonstrated good buffering capability but was not used in subsequent experiments since it was deemed impractical for a continuous process.

Results

a) The rate expression for the catalytic oxidation of thiosulfate is first order with respect to oxygen partial pressure and thiosulfate concentration when either Converter White Metal or Reverbatory Matte are employed as catalysts.

b) The overall activation energies for the Reverbatory Matte and Converter White Metal are 29.0 kJ/mol O_2 (6920 cal/mol) and 32.5 kJ/mol O_2 (7760 cal/mol), respectively.

c) The pseudo-first order rate constants for thiosulfate oxidation in the presence of Reverbatory Matte and Converter White Metal are 1.216×10^{-6} s^{-1} and 2.160×10^{-6} s^{-1}, respectively. Thus at 50°C and under otherwise identical reaction conditions, the Converter White Metal is about 1.8 times more active than the Reverbatory Matte.

d) Under acidic conditions, copper oxide, metallic copper and copper (I) sulfide present in the sulfide catalysts are easily leached into solution to give Cu^{2+}. The leaching process for Cu_2S was found by Gomez-Bueno (23) to be first order with respect

to H^+ and O_2 concentrations. Thus the catalyst itself acts as a sink for the acid produced during the oxidation process (ie. acts as a natural buffering system). For gas uptake experiments, a pH of above 4 is best to minimize leaching (Figure 15 in section 3.2.8).

The Cu^{2+} produced by leaching can react with sulfate at pH levels above about 3 to produce various basic copper sulfate precipitates such as brochantite ($3\ Cu(OH)_2.CuSO_4$) and antherite ($2\ Cu(OH)_2.CuSO_4$). The presence of the brochantite precipitate on the catalyst surface was confirmed by microscopic and x-ray analysis of the sulfides (see Appendix II). These insoluble precipitates account for the poor sulfur mass balances observed in the gas uptake, batch and continuous catalytic oxidation experiments.

e) Both the Reverbatory Matte and Converter White Metal catalysts were reused for further thiosulfate oxidation experiments. The Reverbatory Matte showed a slight decrease in activity on reuse whereas the Converter White Metal showed no decrease at all for such experiments.

6.1.2 Batch Experiments

To get a better understanding of the catalyzed air oxidation of thiosalts, various batch experiments were carried out to obtain product distributions as a function of time.

Operation of Reactor

a) A particle size of 45 to 125 μm was used in most experiments since finer powders are more difficult to remove by settling or

filtration (for analysis of solution); coarser powders are more difficult to suspend and are less effective per unit mass since less catalyst surface area is exposed to the solution.

Results: Synthetic Effluent

a) A possible reaction scheme was postulated from the information contained in various product distribution profiles (see section 4.1.1: reactions (4.1), (4.2), (4.3), and (4.5))).

Thiosulfate can be oxidized to either tetrathionate or sulfate as shown below.

$$2\ S_2O_3^{=} + 0.5\ O_2 + H_2O \xrightarrow{k_1} S_4O_6^{=} + 2\ OH^-$$

$$S_2O_3^{=} + 2\ O_2 + H_2O \xrightarrow{k_2} 2\ SO_4^{=} + 2\ H^+$$

Under basic conditions, the tetrathionate formed in the k_1 step is oxidized to thiosulfate and trithionate.

$$4\ S_4O_6^{=} + 6\ OH^- \xrightarrow{k_3} 5\ S_2O_3^{=} + 2\ S_3O_6^{=} + 3\ H_2O$$

Under neutral or acidic conditions, the trithionate formed in the above step degrades to give thiosulfate, sulfate and acid.

$$S_3O_6^{=} + H_2O \xrightarrow{k_5} S_2O_3^{=} + SO_4^{=} + 2\ H^+$$

These four reaction pathways are substantiated by the anaerobic results described in section 4.1.1.

From the Kinetic Study in which Converter White Metal was employed as catalyst, the rate constants for the various oxidation steps shown above were calculated and are summarized in the following table:

Summary of Kinetic Data for Thioanion Oxidation in the Presence of Converter White Metal: Rate Constants.

Temp. (°C)	k_1 x10^3 (min.$^{-1}$)	k_2 x10^3 (min.$^{-1}$)	k_3 x10^2 (min.$^{-1}$)	k_5 x10^2 (min.$^{-1}$)
30	6.51	0.889	----	1.75
40	4.64	2.00	1.51	2.76
50	4.89	2.22	1.92	----
60	9.99	5.33	3.45	5.93

The corresponding activation energies for the various oxidation processes in the presence of Converter White Metal are shown below:

Summary of Kinetic Data for Thioanion Oxidation in the Presence of Converter White Metal: Activation Energies.

k	E (kJ/mol)	E (kcal/mol)
k_1	43.6	10.4
k_2	49.7	11.9
k_3	36.1	8.6
k_5	34.2	8.2

It should be noted that the rate constants for the k_3 and k_5 steps probably relate to the decomposition of tetrathionate to thiosulfate and trithionate, and to the decomposition of trithionate to thiosulfate and sulfate, respectively, as well as to the oxidation of the thiospecies thus produced. As discussed in section 4.1.1, k_3 and k_5 are therefore <u>not</u> true rate

constants but rather a combination of rate constants.

One would expect k_4 to be much smaller than k_1 and k_2 since the oxidation of $S_4O_6^=$ is relatively slow (ie. in Continuous Studies section, some tetrathionate was usually present even with a residence time of 24 hours). A possible explanation for the large k_4 values is that the initial decrease in $S_4O_6^=$ concentration is due to its rate of absorption onto the catalyst surface rather than its rate of oxidation. After 4 to 6 hours of reaction, the rate becomes zero order in nature, as shown in Figure 19, since it is limited by the slow chemical oxidation of $S_4O_6^=$ and by the number of available sites on the catalyst surface (zero order rate constant, $k_3 = 1.034 \times 10^{-6}$ mol/(L.min.) at 50°C).

The catalyzed oxidation of trithionate is very rapid under acidic conditions as evidenced by the large k_5 rate constants.

The catalytic oxidation steps shown above also appear to apply for the Reverbatory Matte system.

b) In comparing the Reverbatory Matte to the Converter White Metal, one finds that the latter is better at oxidizing all thiosalts thereby producing more sulfate. Since the objective of this work is to design and develop a catalytic system for the complete oxidation of all thiosalts, the Converter White Metal is the catalyst of choice.

c) If the pH is allowed to fluctuate freely during the course of an experiment, it decreases from approximately 10 to 5. The various thiosalt oxidation rates are rather slow under basic conditions. At a set point pH of 5.5, the rate of oxidation of all thiosalts is increased except for the rate of oxidation of

$S_4O_6^=$ which is not easily oxidized under acidic conditions. Decreasing the set point pH to 4.0 further increases the oxidation rates but also increases the leaching of copper into solution (as discussed previously, the leaching rate is first order with respect to H^+ concentration).

Thus, a pH of 5 to 6 is preferred since it is a compromise between high thiosalt oxidation rates and low copper leaching (thereby maximizing catalyst life).

d) The reuse of Converter White Metal in batch type studies indicates that the catalyst shows no loss of activity relative to the initial experiment over an 8 hour period.

e) Increasing the catalyst loading augments the rates of oxidation of all thiospecies since the rate constants are pseudo-first order with respect to catalyst concentration.

f) The use of higher temperatures results in higher oxidation rates. However, the relatively small activation energies shown in Table 9 indicate a rather low temperature dependency on the rates.

g) To achieve higher rates at low temperatures (ie. 30°C) a higher loading (ie. 30 (w/v) %) was employed. The preliminary investigations indicated that these conditions yielded reasonable oxidation rates.

h) The effect of various components likely to be present in real effluent was investigated by preparing different synthetic effluents of varying composition for experiments carried out at 30°C and 30 (w/v) % loading of catalyst.

(i) The addition of Fe^{2+} catalyzes the formation of

trithionate and tetrathionate from thiosulfate thereby slightly increasing the amount of $S_3O_6^=$ and $S_4O_6^=$ in solution.

(ii) The formation of calcium sulfate precipitates does not appear to hinder the catalyst's effectiveness over an 8 hour period.

Results: Real Effluent

a) The synthetic effluent described above and real effluent behaved similarly in batch experiments. Thus, the results obtained with synthetic effluent also apply to real effluent.

b) The reproducibility of duplicate experiments conducted with real mill effluent in the presence of Converter White Metal is very good.

c) A reaction pH of approximately 5.5 was found to be desirable for reasons described previously.

d) The tailings decant solution received from Brunswick Mining and Smelting is low in thiosalt content but high in iron and calcium levels. The Converter White Metal was an effective catalyst for the oxidation of all thioanions present in the tailings decant water.

6.2 Phase II

6.2.1 Continuous Studies

For the continuous catalytic thiosalt oxidation study, a mechanically agitated slurry type reactor was chosen as the best type of continuous flow reactor. This reactor is the easiest to model for experimental purposes, and time limitations did not allow the examination of bed - type reactors.

The overall results show that the oxidation of tetrathionate and trithionate are the limiting factors in reactor performance. Thiosulfate is quickly oxidized to either sulfate or tetrathionate, and the remaining reaction residence time is necessary for the slow oxidation of $S_4O_6^=$ to $SO_4^=$ (this is seen most clearly in the long term batch run (Figure 19). Trithionate oxidation was shown to be much slower in the continuous study (see section 5.2.3.) than in batch experiments (see section 4.1.2) as well. Because of the above, batch and oxygen uptake experiments conducted on a shorter time scale, gave results which were not always applicable to the continuous reactor.

Converter White Metal was chosen as the best overall catalyst on the basis of results obtained from extensive batch and oxygen uptake experiments. For the continuous reactor(s), the optimum parameters using this catalyst can be summarized as follows:

Temperature

For an economically feasible process, the reaction temperature would probably have to be 30°C or less. As noted in

oxygen uptake and batch experiments the overall activation energy is relatively low and so the reaction rate is not unduly sensitive to temperature. This was furthur confirmed in continuous experiments.

Feed Flow and/or
Retention Time

Obviously, the feed flow and retention time are inversely related. The slow oxidation of tetrathionate is a major factor for determination of the reactor retention time. While tetrathionate (and trithionate) formation from thiosulfate can be minimized by utilization of the proper pH, those feeds which already contain appreciable amounts of tetrathionate must have a correspondingly longer reaction time. For feeds of typical mining effluent (8-10 mM $S_2O_3^=$, 1 mM $S_4O_6^=$, and 1 mM $S_3O_6^=$), with a 30 (w/v) % catalyst loading at 30°C and pH = 5, the retention time is about 12 - 13 hours. This provides reactor effluent of about 100 ppm total residual thiosalts (see sections 5.2.2 and 5.2.3).

Reactor pH

The control of the pH of the reaction medium is most important the overall effectiveness of the catalytic oxidation process. Batch results indicated the optimal pH lay between 5 - 6; for the continuous reactor the optimal pH was 5. Below pH 5, the oxidative degradation of the catalyst is excessive (see section 5.2.2) and more tetrathionate is formed from the oxidation of $S_2O_3^=$ by Fe^{+3}, whereas at pH's much above 5, the

oxidation rate is too slow and the buildup of $Fe(OH)_3$ precipitates causes operational problems in the slurry system. In fact even at pH 5 the iron solids build -up is a problem.

Air Flow Rate

The air rate is dependent on the mass transfer coefficient K_La_L , and thus on the reactor design, to insure that the thiosalt oxidation rate is not oxygen transfer limited. With the given reactor design ($K_La_L = 0.03\ sec^{-1}$) and an airflow rate of 10 times the theoretical oxygen requirement, no apparent problems arose. However, no attempt was made to optimize this variable.

O_2 Partial Pressure

The effect of oxygen partial pressure was not investigated in the continuous slurry reactor studies as all such experiments were carried out with atmospheric pressure air. Oxygen uptake experiments, however, indicated a first order dependence in oxygen (see section 3.2.5).

Agitation

This was not studied in detail due to the total number of continuous runs which could be performed. The motor/stirrer combination of 1740 rpm, 10.2 cm dia., 40° pitch, 4 - blade marine propeller gave sufficient agitation with the 30 w/v % slurry loading such that catalyst particles did not settle out. The power input, based on heat dissipation within the reactor, was about 80 watts for 10 L of 30 w/v % slurry with the 1740 rpm stirrer.

Particle Size

While the $\leq$ 45 μm fraction size was chosen in the O_2 uptake experiments to lessen mass transfer effects (see section 3.2.4), a more practical size of $\leq$ 75 μm was chosen for the large scale continuous runs, as much less grinding was required for this fraction. Any mass transfer effects were still minimized and the particles could be more easily settled from the slurry in reactor - settler operation.

Caustic Consumption and Catalyst Life

Since the slow decomposition of the catalyst consumes acid, caustic needed for neutralization of acid produced by thiosalt oxidation is always less than calculated. In fact, for short term runs (< 1 month) no caustic was used at all. As the catalyst ages however, more neutralization is needed to maintain a given set pH.

Because of the oxidative catalyst decomposition, the catalyst life is a function of pH and thiosalt loading. Under given conditions of about 11 - 13 mM thiosulfate with a 5 w/v % loading at a feed rate of 6 - 7 mL/min at pH 5.1 - 5.5, the anticipated catalyst life is probably greater than three months.

Use of Real Thiosalt Mining Effluent

In general, the parameters deduced from running synthetic solutions were also found to give good results with the Brunswick Mining and Smelting Tailings Decant wastewater. The most difficult problem was the buildup of $Fe(OH)_3$ floc within the

reactor. While this did not seem to interfere with catalyst activity, the floc did cause settling problems and would be a major problem in time due to the build-up. This build-up would be a problem with any heterogeneous catalyst unless the oxidation process could be operated at a sufficiently low pH. However, at a low pH the Fe^{3+} catalyzed oxidation of thiosulfate to tetrathionate would become more troublesome.

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APPENDIX I

Mass Transfer Coefficients for Continuous Reactor

For a slurry reactor, the overall rate R (mol/L.sec) of a reaction, at steady state, can be equated to the individual mass transfer steps, i.e.

$$R = K_L a_L (C_L^* - C_L) = K_c a_s (C_L - C_s) = K_s C_s \qquad (A1.1)$$

(first order reaction)

where: K_L = gas - liquid MT coefficient, cm/sec

a_L = specific gas-liquid surface area/liquid volume, cm^{-1}

C_L^* = saturated concentration of gas in liquid phase, mol/L

C_L = concentration of gas in liquid phase, mol/L

K_c = liquid - solid MT coefficient, cm/sec

a_s = catalyst area/liquid volume, cm^{-1}

K_s = surface reaction rate coefficient, sec^{-1}

C_s = surface concentration of gas, mol/L

If only the surface reaction is to be examined (i.e. the intrinsic catalyst activity), then ideally $K_L a_L$ and $K_c a_s >> K_s$ such that $C_s \cong C_L \cong C_L^*$ and the rate is only limited by the catalyst. Typically, when the reactant gas is sparingly soluble in the reaction medium (as in this case), the gas - liquid mass transfer parameter $K_L a_L$ can be small enough that $C_s, C_L << C_L^*$ and thus the rate is mass transfer dependent. Therefore, to insure that this was not a limiting factor in the continuous reactor apparatus, $K_L a_L$ was determined by experiment, and in addition $K_c a_s$ was obtained from correlations.

(1) Determination of $K_L a_L$

The reactor was filled (9L) with a dilute solution of Na_2SO_3 (about 15 mM) and a small amount of $CuCl_2$ added. When air is introduced to the reactor, O_2 is consumed by $SO_3^=$:

$$SO_3^= + 1/2\ O_2 \xrightarrow[Cu^{+2}]{} SO_4^=$$

The above reaction is homogeneous and eqn (A1.1) can be reduced to:

$$-d[O_2]/dt = -\ 1/2\ d[SO_3^=]/dt = K_L a_L(C_L^* - C_L) = K_h C_L$$

where K_h is the homogeneous oxidation rate coefficient. If K_h >>> $K_L a_L$ ($K_h = 5(10^4)$ sec^{-1}, whereas $K_L a_L$ < 1 sec^{-1} (14)), then this reduces to:

$$-\ 1/2\ d[SO_3^=]/dt = K_L a_L(C_L^* - C_L)$$

$$\text{or} \quad K_L a_L = -\ \frac{d[SO_3^=]/dt}{2\ C_L^*} \qquad \text{(A1.2)}$$

Therefore, measuring the concentration of sulfite vs. time will give a linear decrease of slope $2\ C_L^* K_L a_L$.

The analytical results for a series of experiments is shown in Figure A1.1. The sulphite concentration was measured by iodometric titration. All measurements were made using the stainless steel reactor apparatus. A summary of the calculated results is shown in Table A1.1.

Sample Calculation

For Run #1 (see Figure A1.1),

$$\text{slope} = -\ 9.167\ (10^{-6})\ \text{mol}(SO_3^=)/\text{L.sec}$$

then O_2 transfer rate = 1/2 (9.167(10^{-6})) mol/L.sec
= 4.583(10^{-6}) mol O_2/L.sec

solubility of O_2 @ 40°C in H_2O = 1.835(10^{-4}) mol/L (from air sparging, ref.(20)).

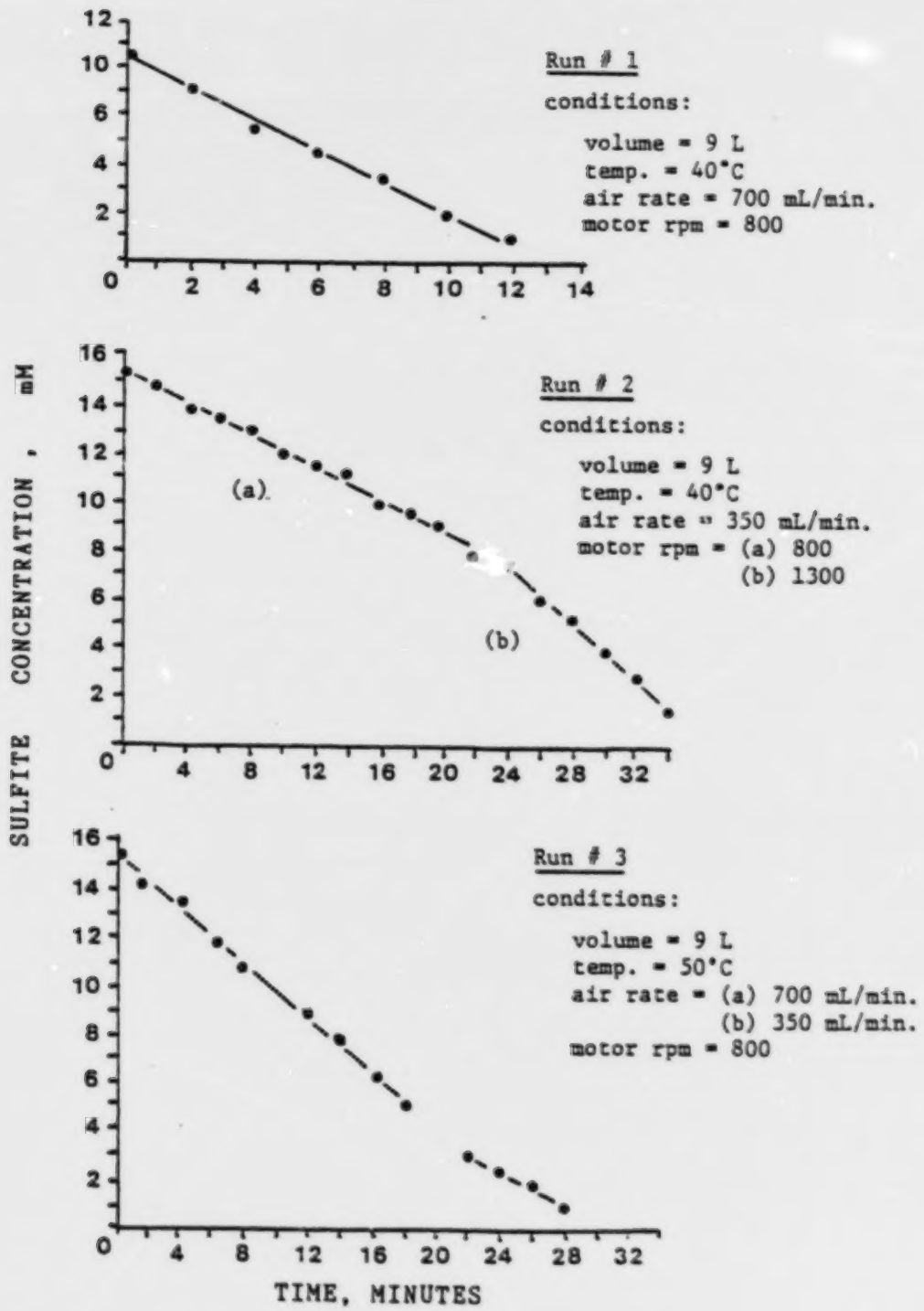

Figure A1.1 Sulphite concentration (mM) vs. time for slurry reactor oxygen mass transfer measurements.

therefore, by eqn. (A1.2):

$$K_L a_L = \frac{9.167(10^{-6})}{2(1.835(10^{-4}))}$$

$$= 0.0250 \text{ sec}^{-1}$$

Table A1.1. Summary of Calculated $K_L a_L$ Coefficients

Run#	air flow, mL/min	temperature ^{o}C	motor rpm	transfer rate, mol/L.sec	$K_L a_L$, sec^{-1}
1	700	40	800	$4.583(10^{-6})$	0.0250
2 (a)	350	40	800	$2.667(10^{-6})$	0.0145
(b)	350	40	1300	$4.425(10^{-6})$	0.0241
3 (a)	700	50	800	$4.765(10^{-6})$	0.0277
(b)	350	50	800	$2.917(10^{-6})$	0.0169

Note that for the above results:

(a) Temperature does not have much of an effect on the transfer rate; the most significant variables are air flow rate and motor rpm. Increasing the air flow rate increases a_L, whereas motor rpm affects both K_L and a_L.

(b) The $K_L a_L$ values are for the homogeneous reaction $SO_3^{=} \longrightarrow SO_4^{=}$, but should be reasonably representative of the heterogeneous slurry especially since the concentration of $SO_3^{=}$, $SO_4^{=}$ is about the same as catalyst experimental runs.

With the above gas - liquid MT coefficients, for a given oxygen demand in thioanion conversion to sulfate, the difference between C_L^* and C_L can be calculated, for example:

Feed flow = 6.1 mL/min of 11.5 mM $S_2O_3^=$, 0.5 mM $S_4O_6^=$, the required O_2 (by eqn. 3.1 and 3.6):

$$\left[\frac{11.5(10^{-3})}{1000} \times 2 + \frac{0.5(10^{-3})}{1000} \times 3.5\right] \times \frac{\text{mol } O_2}{\text{mL}} \times \frac{6.1 \text{ mL}}{10 \text{ L.min}} \times \frac{1 \text{ min}}{60 \text{ sec}}$$

$= 2.516(10^{-7})$ mol O_2/L.sec of oxygen required for complete conversion of thioanions to sulfate.

@ 40°C, 700 mL/min $\quad K_L a_L = 0.0250 \text{ sec}^{-1}$

$C_L^* = 1.835(10^{-4})$ mol O_2/L

Then;

$$2.516(10^{-7}) \text{ mol/L.sec} = 0.0250 \text{ sec}^{-1} [1.835(10^{-4}) \text{mol/L} - C_L]$$

$$C_L = 1.75(10^{-4}) \text{ mol } O_2/\text{L}$$

thus, the difference of C_L from C_L^* is $\frac{1.835-1.75}{1.835} \times 100 = 4.6$ %

This difference is not significant. In the worst case, C_L is 12% less than C_L^*.

(2) Determination of $K_c a_s$

To evaluate K_c, the method employed by Harriot (15) is used, whereby K_c is a function of the terminal settling velocity of the catalyst particle. Here it is assumed that the particle moves with the fluid in turbulent mixing and the only relative motion is due to settling, although there is a correction for agitated tanks. Using these correlations, it was found that $K_c = 0.025$ cm/sec. The specific surface area per volume of slurry, a_s, is estimated using a non-porous spherical particle model. With a particle diameter of 50 μm, slurry loading of 5 w/v %, and

catalyst density of 5.0 gm/cm^3, a_s is about 12 cm^2/cm^3 = 12 cm^{-1}. Therefore, $K_c a_s = (0.0250)(12) = 0.30$ sec^{-1}.

Since $K_c a_s$ is about 10 times as large as $K_L a_L$, this is a less significant resistance, such that $C_L \cong C_s$.

(3) Summary

As expected, there was a small "bottleneck" in oxygen transfer at the gas - liquid interface, but the effect was not significant and the overall catalytic oxidation reaction is not mass transfer limited with the given catalyst activity in this study.

APPENDIX II

Microscopic and X-Ray Analysis of Copper Sulfides

We gratefully acknowledge D. R. Owens and J. E. Dutrizac of CANMET for carrying out a mineralogical study on both the Converter White Metal and Reverbatory Matte (27). The results obtained in this study are briefly summarized below.

Unused Converter White Metal

Figure A2.1 shows the three major phases present in the Converter White Metal. Large grains of copper sulfide (grey) are surrounded by a eutectic of copper sulfide (grey) and copper oxide (black or dark grey). Metallic copper or silver (white or light grey) were evident at the boundaries of the larger copper sulfide grains. The well developed eutectic structure is evident in Figure A2.2 where the light phase is copper sulfide and the darker grey is the copper oxide.

X-Ray diffraction analysis confirmed the presence of Cu_2S (chalcocite type) and Cu_2O (cuprite type).

Electron microprobe analysis of a few grains of each of the major phases yielded the following formulae: $Cu_{2.01}S_{1.00}$ and $Cu_{2.04}O_{1.00}$.

Unused Reverbatory Matte

The photomicrograph in Figure A2.3 indicates that this material is extremely complex. The large, dark grey central areas are similar in appearance to bornite (Cu_5FeS_4) but were found by electron microprobe analysis to have the formula

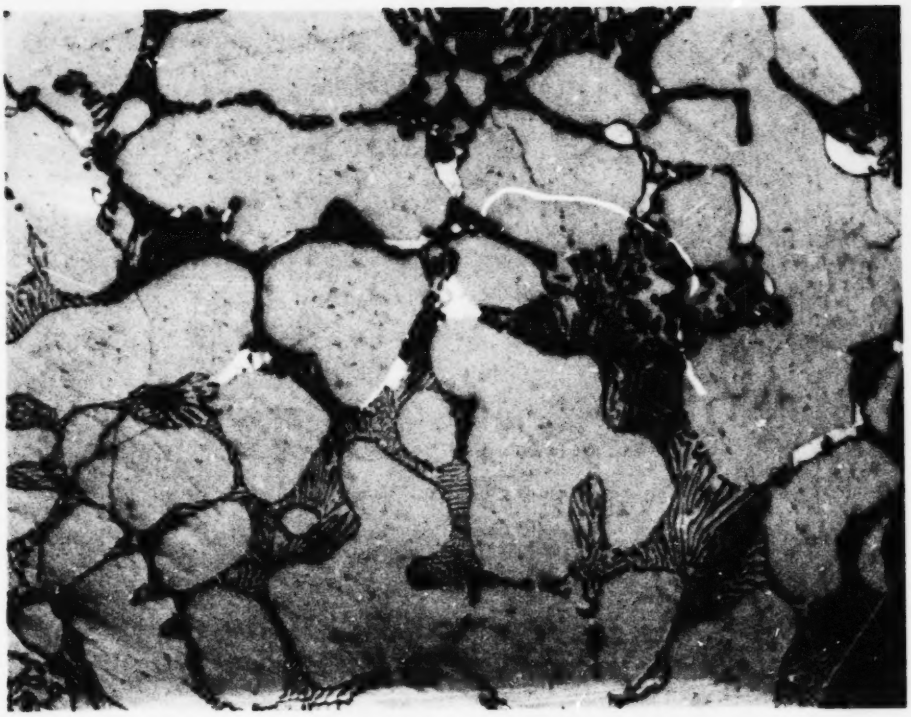

Figure A2.1. Photomicrograph of unused Converter White Metal showing copper sulfide grains (grey) surrounded by a eutectic of copper sulfide (grey) and copper oxide (black or dark grey). (67x).

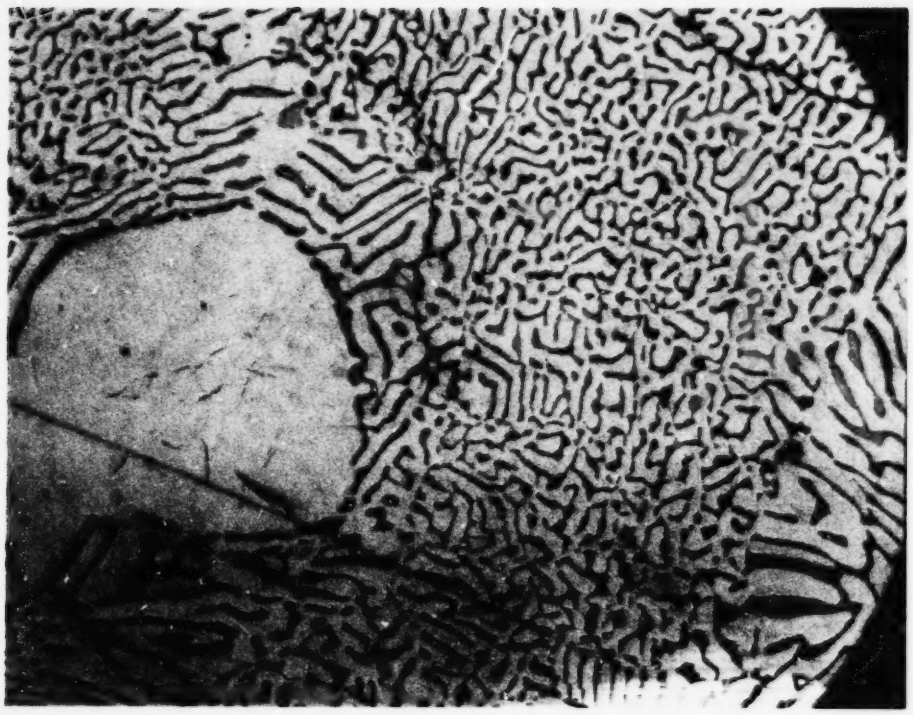

Figure A2.2. Detailed view of unused Converter White Metal shown in Figure A2.1 indicating a eutectic structure of copper sulfide (light grey) and copper oxide (dark grey) surrounding larger copper sulfide grains. (166x).

Figure A2.3. Photomicrograph of unused Reverbatory Matte consisting of different iron-copper sulfides (light and dark grey), iron oxide (dark grey) and metallic copper (white). (266x).

$Cu_{2.87}Fe_{1.06}S_{2.74}$. Within these larger bornite-like grains are fine exsolution lamella of a light coloured phase which is too fine for identification. The light grey major cubanite-like phase contains dark grey exsolution lamella and small blebs of a dark grey phase. Although the light grey phase resembles cubanite ($CuFe_2S_3$), it does not seem to have the proper composition. The dark grey exsolution lamella and dark grey blebs seem to be magnetite (Fe_3O_4).

On the right side of Figure A2.3, are several patches of light grey FeS (iron sulfide: troilite-type) whose composition was found to be by electron microprobe $Fe_{0.97}Cu_{0.04}S_{1.00}$ or $(Fe,Cu)_{1.01}S_{1.00}$.

A few grains of light metallic copper were also evident.

Since the Reverbatory Matte is rapidly cooled, it is quite probable that many of the sulfide phases are metastable assemblages within the Cu-Fe-S-O phase system.

Used Converter White Metal

The used Converter White Metal is similar to that in Figure A2.1 except that the metallic copper has been entirely eliminated and much of the Cu_2O has been leached away. The Cu_2S has been almost entirely altered to digenite ($Cu_{1.8}S$) and djurleite ($Cu_{1.96}S$). The conversion of the Cu_2S to $Cu_{1.80}S$ and $Cu_{1.96}S$ was confirmed by X-ray diffraction analysis.

Used Reverbatory Matte

The used Reverbatory Matte is similar to the unused material (Figure A2.3) except that the native copper has been entirely

eliminated and some of the copper-iron sulfides have been converted to blue covellite ($Cu_{1.1}S$). Microscopically, brochantite ($Cu_4(SO_4)(OH)_6$) was found as a minor phase by X-ray diffraction analysis. The brochantite coats the outside of the grains causing a green colouration.

As discussed extensively in the Results and Discussion section, the acid formed during the thiosalt oxidation is consumed, in the presence of air, by the copper oxide, copper and copper sulfide.

$$Cu_2O + 2\ H_2SO_4 + 0.5\ O_2 \longrightarrow 2\ CuSO_4 + 2\ H_2O \qquad (A2.1)$$

$$Cu + H_2SO_4 + 0.5\ O_2 \longrightarrow CuSO_4 + H_2O \qquad (A2.2)$$

$$Cu_2S + 0.2\ H_2SO_4 + 0.1\ O_2 \longrightarrow Cu_{1.8}S + 0.2\ CuSO_4 + 0.2\ H_2O \qquad (A2.3)$$

Based on the relative proportion of the phases, Cu_2O is the major acid consumer, followed by copper and Cu_2S.

The dissolved copper can be precipitated to give brochantite as shown in equation (A2.4).

$$4\ CuSO_4 + 6\ H_2O \longrightarrow Cu_4(SO_4)(OH)_6 + 2\ H_2SO_4 \qquad (A2.4)$$

Such precipitation provides an explanation for the poor sulfur mass balances in the gas uptake and batch experiments.

After extensive acid attack of the sulfide, the metallic copper and copper oxide are removed. Under acidic pH values, a large buildup of copper is evident in the solution.

APPENDIX IIIA

Mass Transfer: Gas Uptake Apparatus at 50°C

Oxygen must be absorbed from the gas (air) bubbles and be transported by liquid mixing and diffusion to the surface of the catalyst particles. The liquid at the gas-liquid interface is essentially in equilibrium with the gas; the main body of the liquid is at lower oxygen concentration.

At steady state, the rate equations given in Appendix I (expression (A1.1)) may be rearranged to give expression (A3A.1) as extensively discussed by Satterfield (22):

$$\frac{c_e}{N_v} = \frac{d_B}{6K_1H} + \frac{p\,d_p}{6m}\left(\frac{1}{K_c} + \frac{1}{K_s}\right) \qquad \text{(A3A.1)}$$

where c_e = equilibrium concentration of O_2 in the liquid

N_v = molar flux

d_B = gas bubble sphere diameter

d_p = catalyst particle diameter

K_1 = gas absorption coefficient (gas interface to bulk liquid), cm/s

K_c = mass transfer coefficient (bulk liquid to catalyst particle), cm/s

K_s = surface reaction rate coefficient

p = density of catalyst

H = gas holdup in the liquid, cm^3/cm^3 slurry

m = catalyst loading, g cat./cm^3 slurry

Thus, the reciprocal of the rate should be linear with the

inverse of the catalyst weight. Such plots are obtained for both the Converter White Metal and Reverbatory Matte catalyst systems, as shown in Figure A3.1. The intercept is inversely proportional to the gas absorption coefficient, K_l. If the catalyst loading is large (ie. 1/m ---> 0), the rate becomes controlled by the rate of absorption of O_2 at the gas-liquid interface (see section 3.2.3).

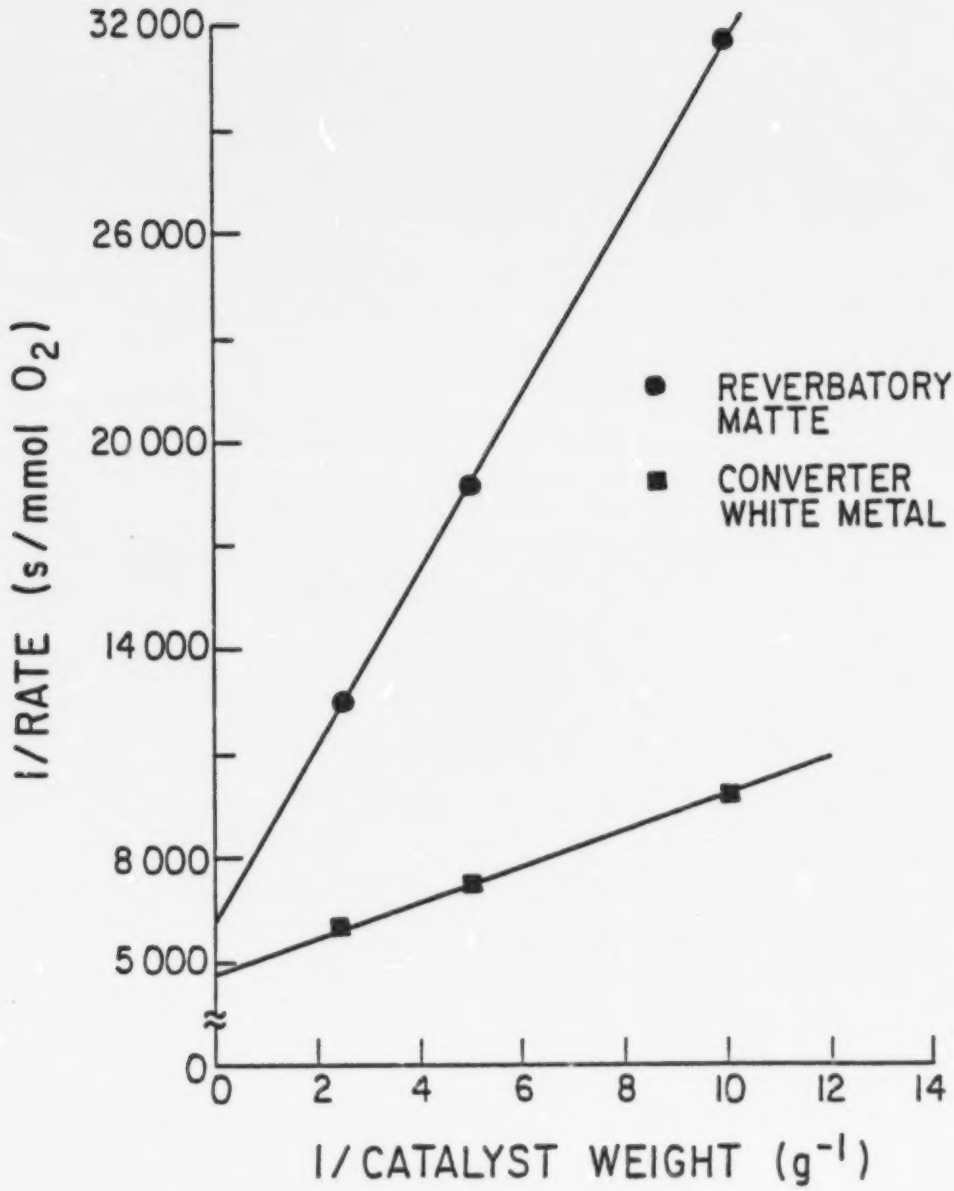

Figure A3.1. Plot of 1/rate versus 1/catalyst weight for Converter White Metal system at 50°C.

APPENDIX IIIB

Determination of Mass Transfer Coefficient for Batch Reactor at 30°C

The gas-liquid mass transfer coefficient for oxygen was determined for the batch reactor by using the method of Okeson and de Waal (14). The results are summarized in Table A3B.1.

Table A3B.1: Summary of Results of Mass Transfer Calculations

Experiment	Conditions		Results	
	air flow (mL/min.)	stirring (rpm)	K_1A_1 (s^{-1})	% O_2 transferred
1	250	300	0.0169	4.3
2	250	700	0.0791	20.3
3	600	700	0.0935	10.0

Generally, temperature does not have much of an effect on the O_2 transfer rate.

In all batch experiments performed in this research:

stirring speed = 700 rpm and air flow > 600 mL/min.

These conditions will yield a K_1A_1 value of 0.0935 s^{-1}; only 10 % of the available oxygen is transferred under these conditions.

APPENDIX IV

Kinetic Study of Converter White Metal

On the basis of the product distribution patterns (at 30°C, 40°C, 50°C, and 60°C) shown in Figure 18, the kinetics of the oxidation of thiosulfate can be studied. It should be noted that it is rather difficult to do a kinetic study of this system due to the inter relation of the various reactions involved in the overall oxidation process.

As discussed extensively in section 4.1.1 (reactions (4.1), (4.2), (4.3) and (4.5)), the four major reactions of interest are:

$$2\ S_2O_3^{=} + 0.5\ O_2 + H_2O \xrightarrow{k_1} S_4O_6^{=} + 2\ OH^- \qquad (A4.1)$$

$$S_2O_3^{=} + 2\ O_2 + H_2O \xrightarrow{k_2} 2\ SO_4^{=} + 2\ H^+ \qquad (A4.2)$$

$$4\ S_4O_6^{=} + 6\ OH^- \xrightarrow{k_3} 5\ S_2O_3^{=} + 2\ S_3O_6^{=} + 3\ H_2O \qquad (A4.3)$$

$$S_3O_6^{=} + H_2O \xrightarrow{k_5} S_2O_3^{=} + SO_4^{=} + 2\ H^+ \qquad (A4.4)$$

The method used to determine the rate expressions and rate constants for these four reactions is similar to the one described by Chanda and Rempel (11).

The rate expressions for reactions (A4.1) to (A4.4) are given in expressions (A4.5) to (A4.8).

$$\frac{d[S_2O_3^{=}]}{dt} = -k_1[S_2O_3^{=}] - k_2[S_2O_3^{=}] + 5/4\ k_3[S_4O_6^{=}] + k_5[S_3O_6^{=}] \qquad (A4.5)$$

$$\frac{d[S_3O_6^{=}]}{dt} = 0.5\ k_3[S_4O_6^{=}] - k_5[S_3O_6^{=}] \qquad (A4.6)$$

$$\frac{d[S_4O_6^{=}]}{dt} = 0.5\ k_1[S_2O_3^{=}] - k_3[S_4O_6^{=}] \qquad (A4.7)$$

$$\frac{d[SO_4^{=}]}{dt} = 2\ k_2[S_2O_3^{=}] + k_5[S_3O_6^{=}] \qquad (A4.8)$$

Figures A4.1, A4.2 and A4.3 show the semilogarithmic plots of the thiosulfate, trithionate and tetrathionate concentrations, respectively, versus time at 30°C, 40°C, 50°C and 60°C. The straight line nature of these plots indicate pseudo-first order kinetics. The slope of the lines are used to estimate the values of the various rate constants.

Expressions (A4.5) to (A4.8) can be simplified by applying the following conditions:

1) Expression (A4.5): Initially, $[S_3O_6^{=}]_o$ and $[S_4O_6^{=}]_o = 0$, therefore the expression simplifies to:

$$\frac{d[S_2O_3^{=}]}{dt} = -(k_1 + k_2)[S_2O_3^{=}] \qquad (A4.9)$$

which upon integration results in expression (A4.10).

$$\ln [S_2O_3^{=}] = -(k_1 + k_2)t + \ln [S_2O_3^{=}]_o \qquad (A4.10)$$

Thus, the slope of a plot of log $[S_2O_3^{=}]$ versus time as shown in Figure A4.1 provides the value of $(k_1 + k_2)$.

2) Expression (A4.6): When $S_3O_6^{=}$ is being formed, $[S_4O_6^{=}] = 0$;

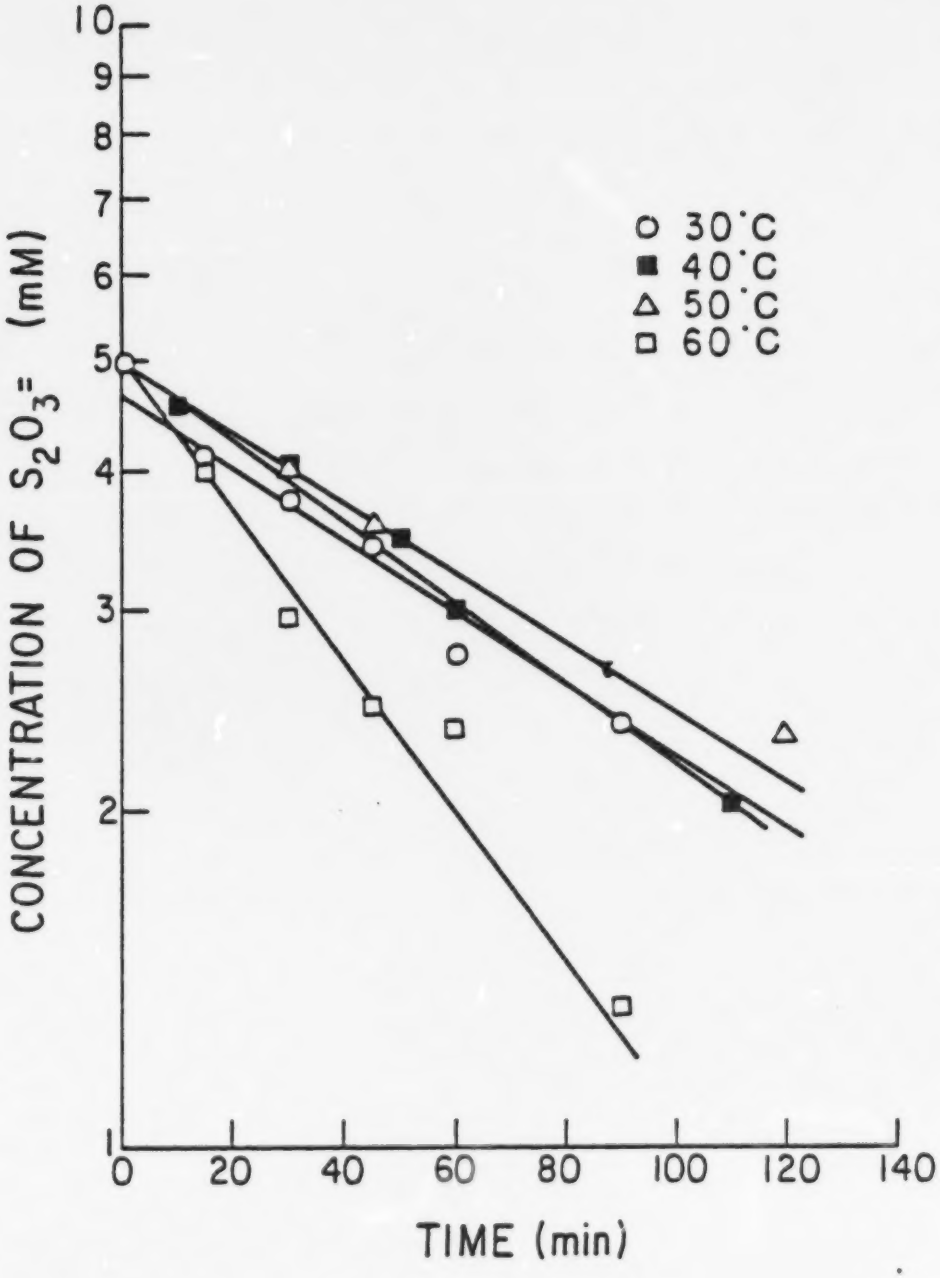

Figure A4.1. Semilogarithmic plot of the decrease of concentration of $S_2O_3^=$ as a function of time in air oxidation catalyzed by Converter White Metal (4 (w/v) % catalyst loading).

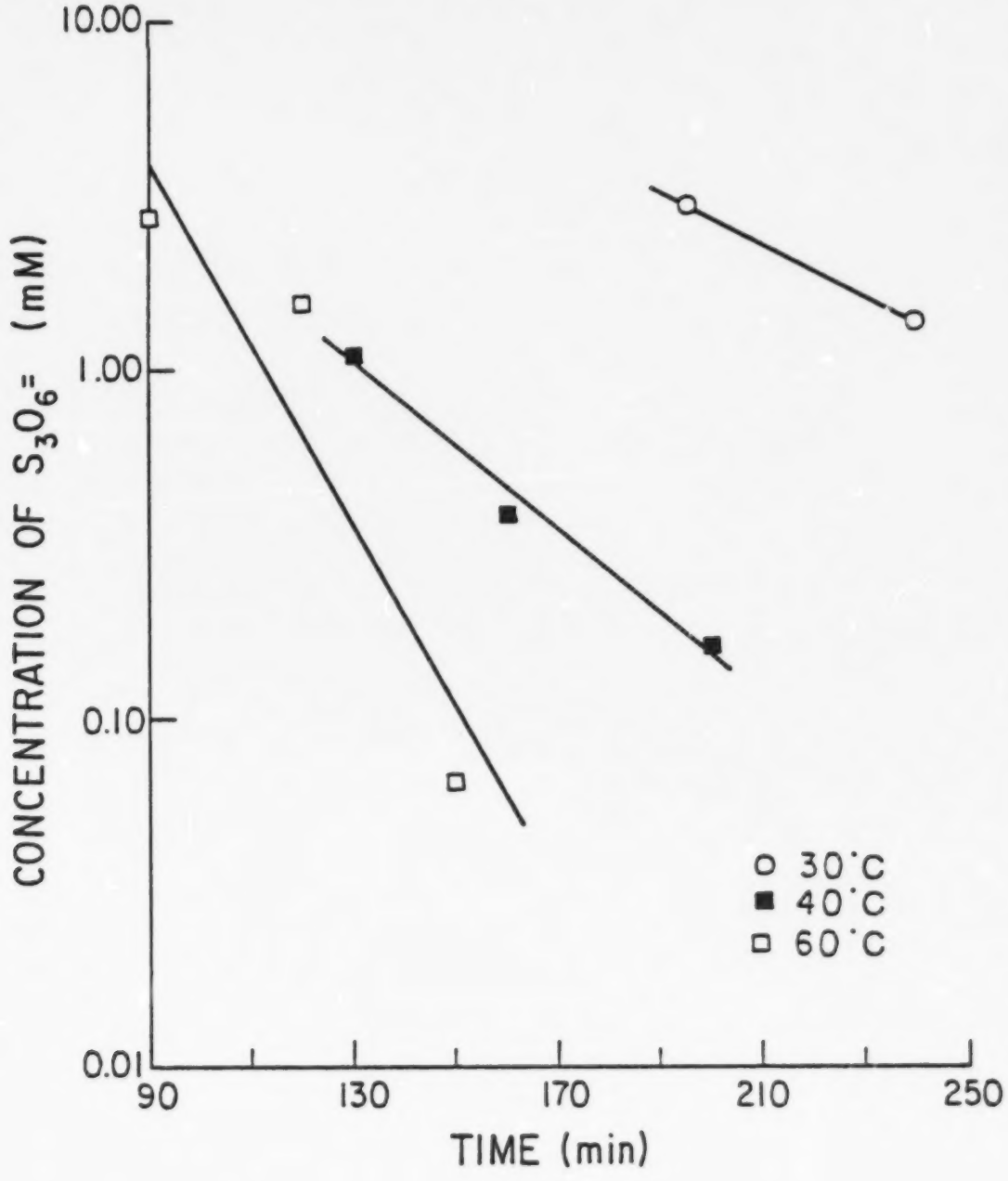

Figure A4.2. Semilogarithmic plot of the decrease of concentration of $S_3O_6^=$ as a function of time in air oxidation catalyzed by Converter White Metal (4 (w/v) % catalyst loading).

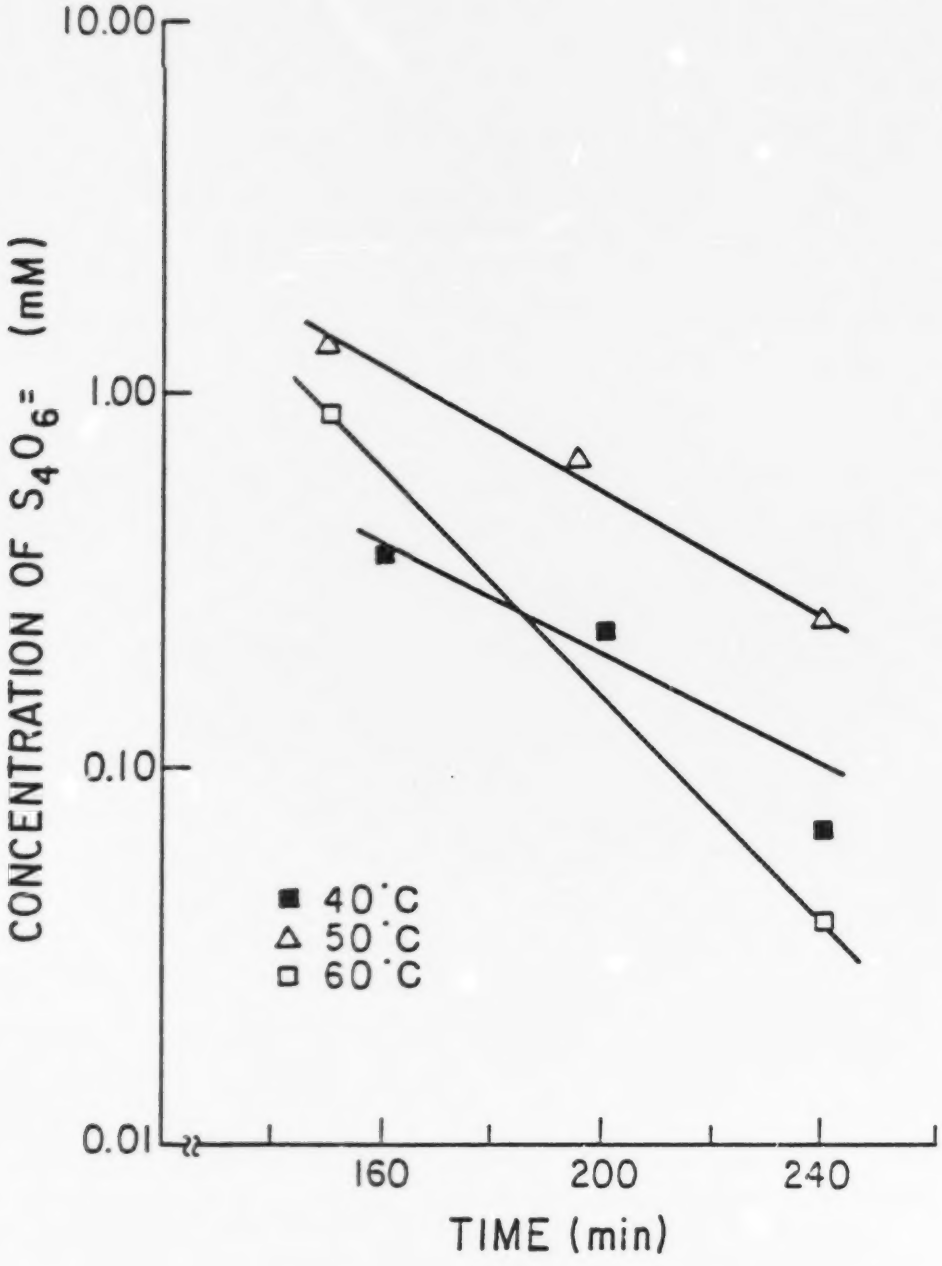

Figure A4.3. Semilogarithmic plot of the decrease of concentration of $S_4O_6^=$ as a function of time in air oxidation catalyzed by Converter White Metal (4 (w/v) % catalyst loading).

thus,

$$\frac{d[S_3O_6^{=}]}{dt} = - k_5[S_3O_6^{=}] \qquad (A4.11)$$

which upon integration provides the expression:

$$\ln [S_3O_6^{=}] = - k_5 t + \ln [S_3O_6^{=}]_o \qquad (A4.12)$$

A plot of log $[S_3O_6^{=}]$ versus time as shown in Figure A4.2 provides the value for k_5.

3) Expression (A4.7): For large t values, $[S_2O_3^{=}]$ is approximately equal to zero. Thus,

$$\frac{d[S_4O_6^{=}]}{dt} = - k_3[S_4O_6^{=}] \qquad (A4.13)$$

which upon integration results in the expression:

$$\ln [S_4O_6^{=}] = - k_3 t + \ln [S_4O_6^{=}]_o \qquad (A4.14)$$

k_3 is calculated from a plot of log $[S_4O_6^{=}]$ versus time as shown in Figure A4.3.

4) Expression (A4.8): Initially, $[S_3O_6^{=}] = 0$ and $[S_2O_3^{=}]_o = 5$ mM. Hence,

$$\frac{d[SO_4^{=}]}{dt} = 2k_2[S_2O_3^{=}]_o \qquad (A4.15)$$

The value of k_2 can be obtained from the initial slopes of the $SO_4^{=}$ curves shown in Figure 18 a to 18 d.

Also, k_1 can be obtained by difference from the $(k_1 + k_2)$ values calculated above.

The values for k_1, k_2, k_3 and k_5 obtained by the foregoing analyses are summarized in Table 8 (see section 4.1.1).

The data in Table 8 may be used to evaluate the activation energies of the various oxidative steps with the Arrhenius function given in expression (A4.16).

$$\ln k = -\left(\frac{E}{R}\right)\left(\frac{1}{T}\right) \qquad \text{where } R = 8.314 \text{ J/mol K} \qquad \text{(A4.16)}$$

The logarithm of the rate constants is plotted as a function of 1/T in Figure A4.4. The activation energies are tabulated in Table 9 (see section 4.1.1).

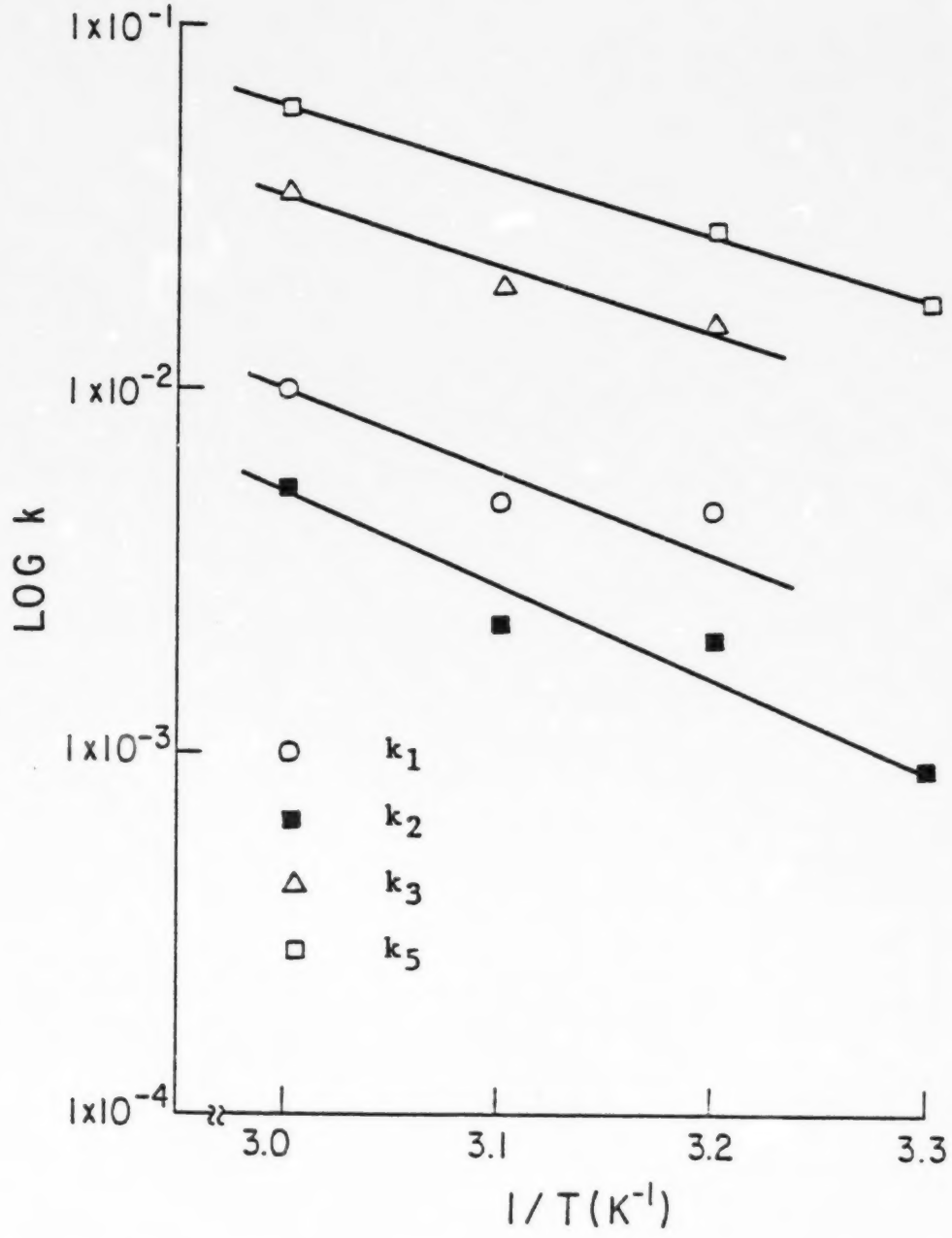

Figure A4.4. Arrhenius plots of pseudo-homogeneous first order rate constants for catalyzed air oxidation of thiosulfate with Converter White Metal (4 (w/v) % catalyst loading).

APPENDIX V

Continuous Reactor Data

APPENDIX V - 1

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample Notes	FEED pH	FEED $S_2O_3^=$ mM	FEED $S_4O_6^=$	FEED S balance	EFFLUENT pH	EFFLUENT $S_2O_3^=$ mM	EFFLUENT $S_3O_6^=$ mM	EFFLUENT $S_4O_6^=$ mM	EFFLUENT $SO_4^=$ mM	EFFLUENT S balance	EFFLUENT Cu ppm	EFFLUENT Fe ppm	EFFLUENT pH reactor	Reactor Conditions	Remarks
Feb 20	11:18		7.8	11.86	(1)	23.7	5.9	0.27	0	1.230	18.2	23.2	ND			T = 50°C	Catalyst 5% w/v loading of Cu_2S catalyst (less than 53 micron)
21	10:00						5.6	0.042	0	0.867	17.6	21.2				air in = 700ml/min	
22	11:00						6.4	0.035	0	0.763	18.4	21.5	ND(2)			motor speed=600rpm	
23								Reactor shut down to change filter screen									
24																feed in = 7 ml/min (10.08L/day)	
25	11:00						4.9	0.033	0	1.130	17.8	22.4					
26	11:30		7.5	11.45	(1)	22.9	6.1	0.080	0	0.778	17.8	21.1	ND			pH set = 6.0	
27	8:45						5.1	0.027	0	1.06	16.2	20.5					
28	10:00						5.2	0.027	0	1.65	17.7	24.4	2			T = 40°C other conditions as above	Iron floc due to corrosion of reactor
29	11:00	Iron floc in					5.7	0.021	0	0.91	17.8	21.5					
Mar 1	10:30	effluent					5.8	0.015	0.492	0.599	17.9	21.9	ND				
2	11:00		7.5	12.04	(1)	24.08	4.6	0.054	0	1.998	17.6	25.7				T = 40°C, feed in = 9.2 ml/min	
3	21:42						7.1	0.462	0	1.947	11.5	20.2	ND				
4	10:30						6.5	0.108	0	2.232	11.0	20.1					
5	9:15						6.9	0.246	0	2.246	9.40	19.3	ND				
6	10.47						6.6	0.204	0	2.60	12.5	23.3					
7	11:15	clear					4.6	0	0	0.099	19.3	18.7	ND		5.7	T = 50°C	(1) for technical grade thiosulfate with $[S_2O_3^=]$ = 11.5mM, $[S_4O_6^=]$ = 0.5mM
8	10:30	"	7.4	10.96	(1)	21.9	4.7	0	0	0.088	18.8	18.8	19.2		5.7	air in = 325 ml/min	
9	11:00	"					4.7	0	0	0.090	18.8	19.2	ND		5.5	feed flow = 6.3 ml/min	
10	10:30	some iron floc in effluent					5.1	0.007	0	0.103	18.6	19.0			5.5	pH set = 5.5	
11	11:30	clear					5.0	0.007	0	0.101	17.5	17.9	ND		5.5	T = 40°C	(2) ND = non detectable
12	8:45	"					5.1	0.007	0	0.626	18.2	20.7			5.5	other conditions as above	
13	10:50	"					5.2	0	0	1.863	16.4	23.9	ND		6.0		
14	10:00	high iron floc					6.4	0.06	0	2.61	11.6	22.2			7.3		* 1 batch
15		"					6.5	0.58	0	2.10	10.10	19.7	ND		7.5		
16		"	7.6	11.07	(1)	22.1	6.5	0.41	0.77	1.91	9.40	20.2			7.3		
17		"					6.7	0.38	0	1.90	10.4	18.8	ND		7.3		
18							6.8	0.38	0	2.0	10.3	19.1			7.3		

APPENDIX V - 2

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample Notes	FEED pH	FEED $S_2O_3^{=}$ gpl	FEED $S_4O_6^{=}$ gpl	FEED S balance	EFFLUENT pH	EFFLUENT $S_2O_3^{=}$ gpl	EFFLUENT $S_3O_6^{=}$ gpl	EFFLUENT $S_4O_6^{=}$ gpl	EFFLUENT $SO_4^{=}$ gpl	EFFLUENT S balance	EFFLUENT Cu ppm	EFFLUENT Fe ppm	EFFLUENT pH reactor	Reactor Conditions	Remarks
Mar 19	9:00						4.4	0.003	0	0.531	17.9	20.0			5.5	T = 50°C	Catalyst - 5% w/v
20	9:30		7.3	11.27		22.5	4.6	0.010	0.242	0.004	17.8	18.6	ND		5.6	air in = 700 ml/min	loading of Cu_2S
21	9:40						4.5	0	0	0	18.4	18.4	ND		5.55	feed flow = 6.1 ml/min	(less than 53 micron)
																pH set = 5.5	
					END OF Cu_2S RUN												
Mar 30							6.4	0.030	0	0.119	16.70	17.2			7.0	T = 50°C	Catalyst - 7.5% w/v
31																air in = 700 ml/min	of converter
Apr 1									REACTOR SHUT DOWN							feed flow = 6.1 ml/min	white metal
2																motor speed = 800 rpm	(less than 53 micron)
3	11:35		7.5	11.86		22.1	6.1	0	0	0.135	15.0	15.54	ND		7.0	pH set = 5.5	
4	10:30						6.2	0	0	0.051	15.6	15.8			7.1		
5	10:30						7.0	0.006	0	0.075	15.4	15.7	ND		6.5		
6	10:30						6.8	0.024	0	0.057	15.6	15.9			6.5		
7	11:15						6.7	0.021	0	0.065	15.4	15.7	ND		6.8		
8	12:15						6.7	0.034	0	0.084	16.3	16.7			6.5		
9	9:45		7.5	11.91		23.8	6.8	0.021	0	0.148	15.9	16.5	ND		6.8		
10	10:30						6.7	0	0	0.174	17.2	17.8			7.0		
11							5.4	0.015	0	0.503	16.4	16.4	ND				
					END OF CMX RUN												
13	13:30	analysed 4/16	7.7	12.31	0.297	25.01	8.7	10.59	0.078	1.050	0.60	26.2	93			T = 50°C	No Catalyst
		reanalysed 4/17	7.6	11.70	0.465	25.26										air in = 700 ml/min	
14	9:30						8.9	13.14	0	0.393	1.40	29.3				feed flow = 6.1 ml/min	evaporation losses
15	12:30						8.9	13.38	0	0.528	0	28.9				motor speed = 800 rpm	cause effluent to be
16	9:30						8.9	13.65	0	0.282	1.00	29.4	ND			pH set = 5.5	approx. 15% more
17	10:00						8.9	13.16	0	0.792	3.00	32.5					concentration.
	10:30	refill	7.6	11.70	0.469												ND = non detectable
18	9:50		7.6	11.88	0.480		8.8	13.012	0	0.711	1.8	30.7					

APPENDIX V - 3

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample Notes	FEED pH	FEED $S_2O_3^{=}$ ppm	FEED Other ppm	FEED S balance	EFFLUENT pH	EFFLUENT $S_2O_3^{=}$ ppm	EFFLUENT $S_3O_6^{=}$ ppm	EFFLUENT $S_4O_6^{=}$ ppm	EFFLUENT $SO_4^{=}$ ppm	EFFLUENT S balance	EFFLUENT Cu ppm	EFFLUENT Fe ppm	EFFLUENT pH reactor	Reactor Conditions	Remarks
Apr 19 -Apr 24			REACTOR SHUT				DOWN										
Apr 25	12:00				$S_4O_6^{=}$ 0.44		6.8	12.14	0	0.66	2.4	29.3				T = 50°C	No Catalyst
26	10:00		7.4	11.03	$SO_4^{=}$ 1.4	25.2	8.7	12.31	0	0.70	3.1	30.5				air = 700 ml/min	evaporation losses
27	10:00						8.7	12.49	0	0.81	1.8	30.0				feed = 6.0 ml/min	cause effleunt to be
28	13:00						8.7	12.78	0	0.73	1.6	30.1				motor rpm = 800 rpm	approx. 15% more
29	12:30				$S_4O_6^{=}$ 0.33		8.9	12.40	0	0.90	1.8	30.2				pH set = 5.5	concentrated
30	10:30		7.6	10.89	$SO_4^{=}$ 1.4	24.5	9.0	12.40	0	0.81	1.8	29.8					
May 1							5.8	0	0.53	0.02	14.6	16.3			6.8	T = 50°C	Catalyst-Reverb Matte
2							5.2	0	0	0	13.4	13.4			5.6	air = 700 ml/min	(less than 53 micron)
3							5.6	0.03	0	0	16.8	16.9			5.5	feed = 6.1 ml/min	5% w/v
4			7.6	11.41	$S_4O_6^{=}$ 0.44	24.6	5.6	0	0	0	15.4	15.4			5.5	motor rpm = 800 rpm	
5							5.6	0	0	0.02	16.8	16.9			5.5	pH set = 5.5	
6							5.5	0	0	0.05	16.4	16.6			5.5		
7							5.3	0	0	0.09	16.8	17.1			5.5		
8			7.7	11.48	$S_4O_6^{=}$ 0.52	25.0	5.2	0.02	0	0.08	18.6	18.9			5.5		
10							5.1	0.02	0	0.08	18.9	19.3			5.5		Sample taken between
11							5.2	0.01	0	0.45	19.6	21.4			5.5		9:30-11:00 unless
12							4.9	0	0	0	18.4	18.4			5.5		otherwise noted
13							no sample taken										
14							5.0	0	0	0.06	18.4	18.7			5.5		

APPENDIX V - 4

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample Notes	FEED pH	FEED $S_2O_3^=$ mM	FEED $S_4O_6^=/SO_4^=$	FEED S balance	EFFLUENT pH	EFFLUENT $S_2O_3^=$ mM	EFFLUENT $S_3O_6^=$ mM	EFFLUENT $S_4O_6^=$ mM	EFFLUENT $SO_4^=$ mM	EFFLUENT S balance	EFFLUENT Cu ppm	EFFLUENT Fe ppm	EFFLUENT pH reactor	Reactor Conditions	Remarks
May 15	10:00						4.9	0.01	0	0.06	18.7	18.9			5.5		Reverb Matte
16			8.1	11.3	1.04	26.8	5.0	0.04	0	0.06	18.6	18.9					less than 53 micron
17							4.9	0.05	0	0.09	18.6	19.0					5% w/v slurry
18				12.1	0.8/1.8	29.3	5.1	0.05	0	0.04	16.6	16.9				50°C	
19					No Sample Taken											feed = 6.1 ml/min	
20							4.9	0.06	0	0.01	18.2	18.4					
21							4.9	0	0	0	19.1	19.1				pH set = 5.5	
22							4.8	0	0	0	19.1	19.1					
23							4.8	0.05	0	0.03	19.1	19.3					
24							4.8	0	0	0.04	18.5	18.6					
July 6	10:00		7.6	11.2	$S_4O_6^=$ 0.5	24.4	4.2	0	0	0.19	16.0	16.8			6.2		CNH catalyst (reused)
7							4.2	0	0	0.22	14.0	14.9	ND				5% w/v
8							5.3	0.01	0	0.62	15.4	17.9			5.8	T = 50°C	
9							4.0	0	0	0.13	16.4	16.8	ND		6.1	feed = 6 ml/min	
10							6.0	0	0	0.05	15.2	15.4				air = 700 ml/min	
11							5.5	0	0	0.66	12.8	15.4				pH set = 5.5	
12							6.0	0	0	0.65	13.6	16.2	ND			(PVC Reactor)	
13							6.0	0	0	0.47	13.4	15.2					
14							6.0	0	0	0.48	13.2	15.1					
15							6.1	0	0	0.48	13.2	15.1	ND				

APPENDIX V - 5

CONTINUOUS REACTOR DATA

Date Time (1984)	Sample Notes	FEED pH	FEED $S_2O_3^=$ gpl	FEED $S_4O_6^=$, $S_3O_6^=$	FEED $SO_4^=$ gpl	FEED S bal.	EFFLUENT pH	EFFLUENT $S_2O_3^=$ gpl	EFFLUENT $S_3O_6^=$ gpl	EFFLUENT $S_4O_6^=$ gpl	EFFLUENT $SO_4^=$ gpl	EFFLUENT S bal.	EFFLUENT Cu ppm	pH reactor	Reactor Conditions	Remarks
July 16							6.2	0	0	0.52	12.7	14.8				
17							5.6	0	0	0.30	13.8	15.0	ND			
18		7	11.3	$S_4O_6^=$ 0.41	0.9	24.8	4.7	0	0	0	18.2	18.2	22	5.1	T = 50°C air = 700 ml/min feed = 6 ml/min pH = 5.1 (set) 5% w/v CNH less than 75 micron	7/17 21.9 ppm Zn^{+2} 5.3 ppm Pb^{+2} 3.5 ppm Ag^{+} added to feed
19							5.1	0.02	0	0	18.4	18.4	5			
20							5.1	0	0	0	18.7	18.7				
21							5.1	0	0	0	18.7	18.7	11			
22							5.1	0	0	0	18.7	18.7	10			
23							5.1	0	0	0	18.6	18.6				
24							5.1	0	0	0	18.5	18.5				
25							5.1	0	0	0	19.4	19.4	68			
26							5.1	0	0	0	19.4	19.4	66			
27							5.1	0	0	0	18.5	18.5	66			
28							5.1	0	0	0	18.5	18.5				
29							5.1	0	0	0	18.5	18.5	85			
30							5.1	0	0	0	18.6	18.6	70			
31							5.1	0.08	0	0	18.0	18.1				
Aug 1							5.1	0	0	0	16.8	16.8	94			
2							5.1	0	0	0	16.8	16.8	55			
3 10:00							5.1	0	0	0	19.6	19.6	72			
3 2:30		7	18.2	$S_4O_6^=$ 1.22			5.1	0.07	0	0.93	31.8	35.6				8/3 - 1:30 feed changed to 2000 ppm $S_2O_3^=$
3 7:00							5.1	0	0	0.50	34.2	36.2				
4							5.1	0	0	0.27	25.0	26.1	114			
5							5.1	0	0	0.31	28.1	29.3				
6							5.1	0.02	0	0.35	27.7	29.1	81			
7							5.1	0.02	0	0.31	27.7	28.9	89			
8											26.8					
9											27.8					

APPENDIX V - 6

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample Notes	FEED pH	FEED $S_2O_3^{=}$ mM	FEED $S_4O_6^{=}$ mM	FEED $SO_4^{=}$ mM	FEED S bal.	EFFLUENT pH	EFFLUENT $S_2O_3^{=}$ mM	EFFLUENT $S_3O_6^{=}$ mM	EFFLUENT $S_4O_6^{=}$ mM	EFFLUENT $SO_4^{=}$ mM	EFFLUENT S bal.	EFFLUENT Cu ppm	EFFLUENT Fe ppm	pH (reactor)	Reactor Conditions	Remarks
Sept 11	9:00-10:00		6.5	14.71	0.63	3.1	35.0	5.2	0	0	0.486	14.40	16.34			as in sample pH	Temp = 30°C	CRH Catalyst (75 m)
12								5.3	0	0	0.882	16.80	20.33					
13								4.9	0	0.250	0.92	17.10	21.53	0*			Feed Flow=12.4 ml/min	-30% wt/vol loading
14		Feed analyzed 9/18	6.0	14.2	1.9	4.6	40.6	7.6	3.5	4.6	0.04	13.2	34.6		problem with feed pump		Air Flow = 150 ml/min (@ STP)	- Temp. const.
15																		- air variable
16								5.0	0	1.34	1.87	16.7	28.2	0*	0	6.0		Feed Composition:
17								5.5	0	0.37	1.27	16.7	22.9			6.4		$[S_2O_3^{=}]$ = 1600 ppm
18								5.3	0	0.36	0.98	16.2	21.2	0*	0	6.3		$[S_4O_6^{=}]$= 200 ppm
19								4.0	0	0	1.17	18.9	23.6	89		5.5		50 ppm Fe^{+2} (as $FeSO_4$)
20			3.2	12.5	0.2	8.6	46.2	4.5	0	0	1.27	18.6	23.7	102		5.4		22 ppm Zn^{+2})
21								4.1	0	0	1.33	18.1	23.4	123	5	5.1		5 ppm Pb^{+2}) as NO_3^-
22			3.5	12.8	1.2	8.7	43.0	4.2	0	0	1.61	18.1	24.5	179		5.1	09/21 air flow 300 ml/min (@STP)	3 ppm Ag^{+}) forms
23																		pH 3-5 (added H_2SO_4)
24								4.3	0	0	1.80	18.5	25.7	166	0			
25	10:00							4.6	0	0	1.83	18.9	26.2	51	4	5.1	09/23 air flow 150 ml/min effluent filtered samples 09/23-26 became progressively more yellow & turbid on sitting. A fine dark ppt. formed too	
25	4:00		5.6	13.7	1.57	8.3	43.9	-	-	-	-	-	-	-	-	-		
26								4.0	0.14	0.27	2.35	17.6	28.1	68	6	5.1		pH setpoint of reactor lowered to 4.0 09/25
								3.7	0.18	0	2.10	15.5	24.3	151	16	5.2		
								3.6	0.18	0.33	1.24	17.5	23.8	138	32	5.0	09/26 3:00 lowered pH set to 4:00	09/26 2:30 H_2SO_4 (1:1) sol'n added by pH controller to maintain pH = 4.00
27		effluent bluish	5.0	11.6	3.19	8.2	44.2	3.1	0	0	1.11	39.0	43.4	1057	129	4.0		09/27 pH maintained by addition of 1M H_2SO_4

APPENDIX V - 7

CONTINUOUS REACTOR DATA

			FEED					EFFLUENT									
Date (1984)	Time	Sample Notes	pH	$S_2O_3^=$ mM	$S_4O_6^=$	$SO_4^=$ mM	S bal.	pH	$S_2O_3^=$ mM	$S_3O_6^=$ mM	$S_4O_6^=$ mM	$SO_4^=$ mM	S bal.	Cu ppm	Fe ppm	pH (reactor)	Reactor Conditions	Remarks
Oct 28		some samples turbid (yellow)						3.1	0	0.05	1.56	19.5	25.8	176	118	4.0	recalibrated pH probe (replaced)	09/28 - pH maintained by add'n of 1M H_2SO_4
29		with time due						3.6	0.04	0.174	2.60	21.0	32.0	136	80	3.8		
30		to formation						4.2	1.21	2.106	2.79	19.5	39.4	91	66	3.8		
1		of Fe^{+3}	4.6	13.5	1.95	8.3	43.8	3.7	0.66	1.56	3.26	16.5	35.6	59	60	3.7		* not detectable by ammonia method
2								3.5	0.17	0.2	3.06	17.6	30.8	76	69	3.4		
3	10:00							7.8	8.26	4.67	0	11.9	42.4	51	2	7.5		
4			3.5	14.5	1.58	8.3	43.6	5.3	5.56	5.96	0.6	13.5	44.9	250	36	5.0	air increased to 600 ml/min	
5								6.0	4.31	3.96	1.60	12.9	39.8	133	4	6.0	←	
Oct 6								8.5	8.54	6.36	0	10.5	46.7	183	3	7.9	H_2SO_4 added to lower pH (1M)	
7	5:15		3.5	13.3	1.82	5.3	39.2	4.0	0.07	0.68	5.184	15.9	38.8	170	2	4.9	←	
8								5.0	0.82	0	3.55	14.8	30.6	72	45	5.0		
Oct 9								5.0	4.81	4.24	1.34	9.1	36.2	230	13	5.0		
10								4.9	2.51	2.36	3.92	9.1	37.7		6			
11								7.8	7.32	5.65	0.71	10.0	44.4		2			

APPENDIX V - 8

CONTINUOUS REACTOR DATA

Date (1964)	Time	Sample Notes	FEED pH	FEED $S_2O_3^=$ mM	FEED $S_4O_6^=$ mM	FEED $SO_4^=$ mM	FEED S bal.	EFFLUENT pH	EFFLUENT $S_2O_3^=$ mM	EFFLUENT $S_3O_6^=$ mM	EFFLUENT $S_4O_6^=$ mM	EFFLUENT $SO_4^=$ mM	EFFLUENT S bal.	EFFLUENT Cu ppm	EFFLUENT Fe ppm	EFFLUENT NaOH Used	EFFLUENT pH (reactor)	Reactor Conditions	Remarks
Oct 18	10:00	sample from reactor filtered through Whatman #40 paper	4.5	13.55	2.2	6.8	42.7	4.9	0	0.85	1.26	16.30	23.9		3.6	nil	5.6	T = 30°C air = 300 ml/min feed = 12 ml/min pH set = 5.0 Stirred rpm = 1740	CNH - 30 wt/vol % - 75 m Feed: $[S_2O_3^=]$ = 1600 ppm $[S_4O_6^=]$ = 200 ppm 50 ppm Fe^{+2} pH 3-5 (added H_2SO_4) 22 ppm Zn^{+2} 5 ppm Pb^{+2}
19								5.0	0.02	0	1.15	17.2	21.8		2.8		5.2		
20								5.0	0	0	1.04	18.6	22.8		3.6		5.12		
21								5.1	0	0	0.93	17.6	21.3		3		5.1		
22			5.0					4.8	0	0	0.95	17.0	20.8		2		5.15		
23								5.5	0	0	0.97	19.6	23.5		1		5.38		
24								5.0	0	0	0.91	18.0	21.6		0.7		5.55		
25			4.5	14.4	1.9	3.2	39.7	5.4	0	0	0.92	16.4	20.1		0.7		5.70		
26								6.3	0.02	0	0.86	16.4	19.9		0.7		6.50		
27								6.2	0	0	0.92	16.4	20.1		0		6.15		
28			4.1	8.64	1.3	2.5		6.3	0	0.24	0.88	17.0	21.2		0		6.10	← feed changed to 1000 mg/L $S_2O_3^=$, 200 mg/L $S_3O_6^=$, 200 mg/L $S_4O_6^=$ adding H_2SO_4 (1M) to lower pH	
29							27.9	6.5	0	0.35	0.84	12.8	17.2		0		6.5		
30								5.2	0	0.05	0.17	15.2	16.0		1		5.19		
31								5.15	0	0.12	0.32	14.8	16.4		0.9		5.19		
Nov 1			3.8	8.35	1.5	3.4		- reactor breakdown -											
2								6.4	0	0.498	0.86	10.4	15.3		0		6.68		
3								6.8	0	0.63	1.18	10.7	17.3		0		6.55		
4			4.2	8.66	1.4	3.0		7.1	0	0.85	0.84	11.2	17.1		0		6.68		
5								6.8	0	0.94	1.16	10.1	17.6		0		6.80		
6								6.6	0	0.86	1.39	10.5	18.6		0		6.54		

END OF RUN

APPENDIX V - 9

CONTINUOUS REACTOR DATA

			FEED					EFFLUENT											
Date (1984)	Time	Sample Notes	pH	$S_2O_3^=$ mM	$S_4O_6^=$ mM	$SO_4^=$ mM	S bal.	pH	$S_2O_3^=$ mM	$S_3O_6^=$ mM	$S_4O_6^=$ mM	$SO_4^=$ mM	S bal.	Cu ppm	Fe ppm	Ce^{+2} mM	pH (reactor)	Reactor Conditions	Remarks
Nov 13	noon	material as received		'Tailings Decant' Water														air flow = 350 ml/min feed flow = 15 ml/min T = 30°C	Feed: Brunswick Tailings Decant Water Catalyst: 30 wt/vol% CWH ≤ 75μm
14								5.6	0	0.20	0.126	25		49	1.4	11.8	5.6		
15								5.5	0	0.03	0.237	20.7		-	-	13.6	5.3		
16								6.0	0	0.17	0.288	24.8		6	0.4	13.6	6.1		
17								6.0	0	0.21	0	24.0		47	0.5	13.0	-		
18								7.0	0	0.08	0.13	23.2		4	0	13.0			
19								8.1	0	0.66	0.19	21.4		4	0	12.4	8.2		
19	4:00							4.0	0	0	0	25.9		4,167	72	11.8	4.0	*1M H_2SO_4 added to control pH	
20								4.0	0	0	0	25.9		3,196	36	12.8	4.0		
20	8:00							4.0	0	0	0.05	25.6		2,560	31	12.7	4.0		
								END OF RUN											

APPENDIX V - 10

CONTINUOUS REACTOR DATA

Date (1984)	Time	Sample / Notes	FEED	EFFLUENT pH	$S_2O_3^=$ mM	$S_3O_6^=$ mM	$S_4O_6^=$ mM	$SO_4^=$ mM	S bal.	Cu ppm	Fe ppm	Ca^{+2} mM	pH (reactor)	Reactor Conditions	Remarks
Dec 10	2:00	Start	'Tailings Decant' Water											30 wt/vol% CHH	* feed analysis Dec 11
11	10:15	filtered sample		7.7	0	0.82	0.12	17.7	20.6	26	0.6	10.7	7.76	T = 30°C	$[S_2O_3^=]$ - 2.08mM
12				6.7	0	0.51	0.15	20.0	22.1	8.5	1.3	12.0	6.98	feed flow=15ml/min	$[SO_4^=]$ - 17.8mM
13				6.9	0	0.47	0.18	19.0	21.1	12.8	0.8	11.0	7.4	air flow=250ml/min	
14				7.1	0	0.49	0.17	17.6	19.8	8.5	0.5	11.2	7.4	pH(lower limit) 5.5	$[S_4O_6^=]$ - 0.49mM
15				-	-	-	-	-	-	-	-	-	-	* pump feed left off overnight, no sample taken	Fe - 488 ppm
															$[S_3O_6^=]$ - 0.58mM
Dec 16				7.3	0	0.49	0.35	16.8		0	0.3		7.3		Ca^{+2} - 490 mM
17				7.3	0	0.37	0.45	16.8		0	0.6		7.26		Cu^{+2} - nil (12.2mM)
18				6.9	0.03	0.28	0.51	18.2		0	1.3		7.2		[Total S] = 27.7mM
															pH = 6.1
19				7.2	0	0.22	0.48	17.8		0	1.3		7.4		Feed analysis (setting 3 days at room temp)
20				6.2	0.02	0.23	0.26	18.8		34	1.2		6.1		$[S_2O_3^=]$ = 2.58 mM
21				7.3	0	0.28	0.46	19.0		0	1.1		7.0	* air delivery tube plugged up	$[S_3O_6^=]$ = 0.598 mM
															$[S_4O_6^=]$ = 1.067 mM